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Use of the Flame Photometric Detector Method for Measurement of Sulfur Dioxide in Ambient Air

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This document is to be used in conjunction with the instrument manufacturer's instruction manual. The document consists of six sections: (1) Introduction to FPD principle, (2) Installation and startup of the analyzer, (3) Calibration sources and their air supplies, (4) Procedures for multipoint dynamic calibration, (5) Procedural aids, and (6) References and Index.

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USE OF THE FLAME PHOTOMETRIC DETECTOR METHOD FOR MEASUREMENT OF SULFUR DIOXIDE IN AMBIENT AIR

A TECHNICAL ASSISTANCE DOCUMENT

by

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DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

Sulfur dioxide is a pollutant for which national primary and secondary ambient air quality standards have been established by the Environmental Protection Agency. In order to insure that the standards (as specified in the Code of Federal Regulations (CFR) Title 40, Chapter I, Part 50) are not exceeded, continuous monitoring is sometimes used.

This technical assistance document (TAD) is intended to serve as a sourcebook of information and outlines of good practices for operation and calibration of SO_2 analyzers based on the measurement principle of the flame photometric detection (FPD) method. Critical parameters are identified which affect the operation and calibration of FPD analyzers. This document can be used with older analyzers which measure "total" sulfur, as well as newer models which are improved in specificity for SO_2 and have been designated as "equivalent methods" by EPA.

The reader should note that the techniques for generation of SO_2 calibration standards and zero air (discussed in Section 3.0) may be used in conjunction with any ambient air SO_2 analyzer, not just FPD SO_2 analyzers.

Many of the items discussed in this document are based on findings from a literature search, interviews and communications with FPD manufacturers and users, results of laboratory calibrations and experiments, and trial field use of the document.

This document is to be used by technical personnel in conjunction with the manufacturer's instruction manual and the appropriate sections of EPA *Quality Assurance Handbook for Air Pollution Measurement Systems* - Volume II (EPA-600/4-77-027a).

This TAD is divided into six major sections: introduction, installation and startup of an FPD SO_2 analyzer; generation of SO_2 calibration standards and zero air; calibration of the FPD; procedural aids; references and index.

It is recommended that the user of this document first read it entirely and make note of points which relate to his specific brand of analyzer. Index tabs can be attached to pages of special interest so they can be found again quickly. Note that precautionary or emphasized material in this document is set apart from the text by being enclosed in "boxes."

The user's attention is called particularly to the following topics covered in this document:

Topic	**Section**
Nonequivalent FPD analyzers	1.3.3
Temperature and humidity control	2.2.2
Ambient air sampling	2.2.4
Safe use of hydrogen	2.3.3, 2.3.4
Generation of calibration standards and zero air	3.0
Carbon dioxide interferences	3.6.3
Zero, span, and multipoint calibration	4.0
Airflow measurements and corrections	5.0

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ABSTRACT

This Technical Assistance Document is intended to serve as a source-book of information and outlines of good practice for operation and calibration of ambient air SO_2 detection analyzers based on the measurement principle of Flame Photometric Detection (FPD). This is accomplished through the identification and control of critical parameters affecting the operation and calibration of FPD analyzers. The document may be used with analyzers which measure total sulfur, as well as with new SO_2-specific models which have been designated as equivalent methods by EPA.

This document is to be used in conjunction with the instrument manufacturer's instruction manual. The document consists of six sections: (1) Introduction to FPD principle, (2) Installation and startup of the analyzer, (3) Calibration sources and their air supplies, (4) Procedures for multipoint dynamic calibration, (5) Procedural aids, and (6) References and Index.

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SECTION 1.0

INTRODUCTION

1.1 FLAME PHOTOMETRIC DETECTION OF SULFUR: BASIC PRINCIPLES

Many elements give characteristic emission spectra when burned in a flame. Absorption of energy from the flame allows a ground-state atom or molecule to reach a higher energy level or an excited state. The excited-state atom or molecule contains excess energy and may return to its ground state by emitting light. The wavelength and intensity of this light are the basis for selective and quantitative analysis of different elements or compounds.

When a sulfur-containing compound (inorganic or organic) is burned in a flame, a minor product is the excited-state diatomic molecular sulfur species, S_2^*. The asterisk (*) indicates the species is excited, that is, has energy in excess of that of the unexcited, ground-state, S_2 species. The S_2^* species is inclined to seek a lower energy level and one mechanism by which S_2^* reverts to its ground state is by a chemiluminescent process. By this process light energy is emitted with the spectral characteristics shown in Figure 1.1.[1,2,3] Two equations describing this are:

$$\text{sulfur-containing molecules} \xrightarrow[\text{in flame}]{\text{burn}} S_2^* \qquad (1)$$

$$\underset{\text{(excited electronic state)}}{S_2^*} \longrightarrow \underset{\text{(normal electronic state)}}{S_2 \quad + \text{light, } h\nu} \qquad (2)$$

The left-hand side of equation 2 shows the excited state S_2^* species. The right-hand side shows the products of the decomposition of S_2^*. The products are the unexcited S_2 species and a quantity of light energy, i.e., photons (hence the name "photometric" detector). The "detector" portion of the flame photometric detector is a photomultiplier tube, which senses the light energy emission intensity and converts it to an equivalent electrical current which is proportional to the original concentration of SO_2 (or other sulfur-containing gas) in the air sample.

The S_2 emission system is broad-based and falls mainly in the region 2,769 to 6,166 Å. Figure 1.1 shows a portion of the emission spectrum. The peak of the spectrum is around 380 nm (3,840 Å). Narrow-band pass filters are commonly used in detector assemblies to allow only light near the peak region to pass.

The formation of the S_2 molecule in the flame occurs when two S atoms combine in the presence of a "third body" (denoted by M), equation 3:

$$S + S + M \qquad S_2 + M. \tag{3}$$

Hydrogen and hydroxyl radicals, also produced by the flame, react with S_2 to produce the excited state $S_2{}^*$ species[4,5,6] (equations 4,5).

$$H + H + S_2 \qquad S_2{}^* + H_2 \tag{4}$$

$$OH + H + S_2 \qquad S_2{}^* + H_2O \tag{5}$$

The intensity of the chemiluminescence or light produced by $S_2{}^*$ as described by equation 2 is proportional to the $S_2{}^*$ concentration, $[S_2{}^*]$, equation 6:

$$\text{light intensity} = k\,[S_2{}^*]. \tag{6}$$

As stated above, formation of S_2 depends on reaction between two S atoms in the presence of a third body, M (another gaseous atom or molecule). For reaction to occur, the two S atoms must collide simultaneously with M. It can be shown that the number of collisions (and therefore potential reactions between two sulfur atoms) is proportional to the square of their concentration.[7]

Therefore the rate of formation of the $S_2{}^*$ molecular species will be proportional to the square of the S atom concentration, equation 7, which in turn depends on the concentration of the sulfur-containing molecule.

$$\frac{\Delta\,[S_2]^*}{\Delta\ \text{time}} = k\,[S]^2 \tag{7}$$

Thus, for a continuous SO_2 analyzer based on flame photometry, the light energy produced by decaying $S_2{}^*$ and received by the photomultiplier tube is predicted to be proportional to the square of the SO_2 concentration.

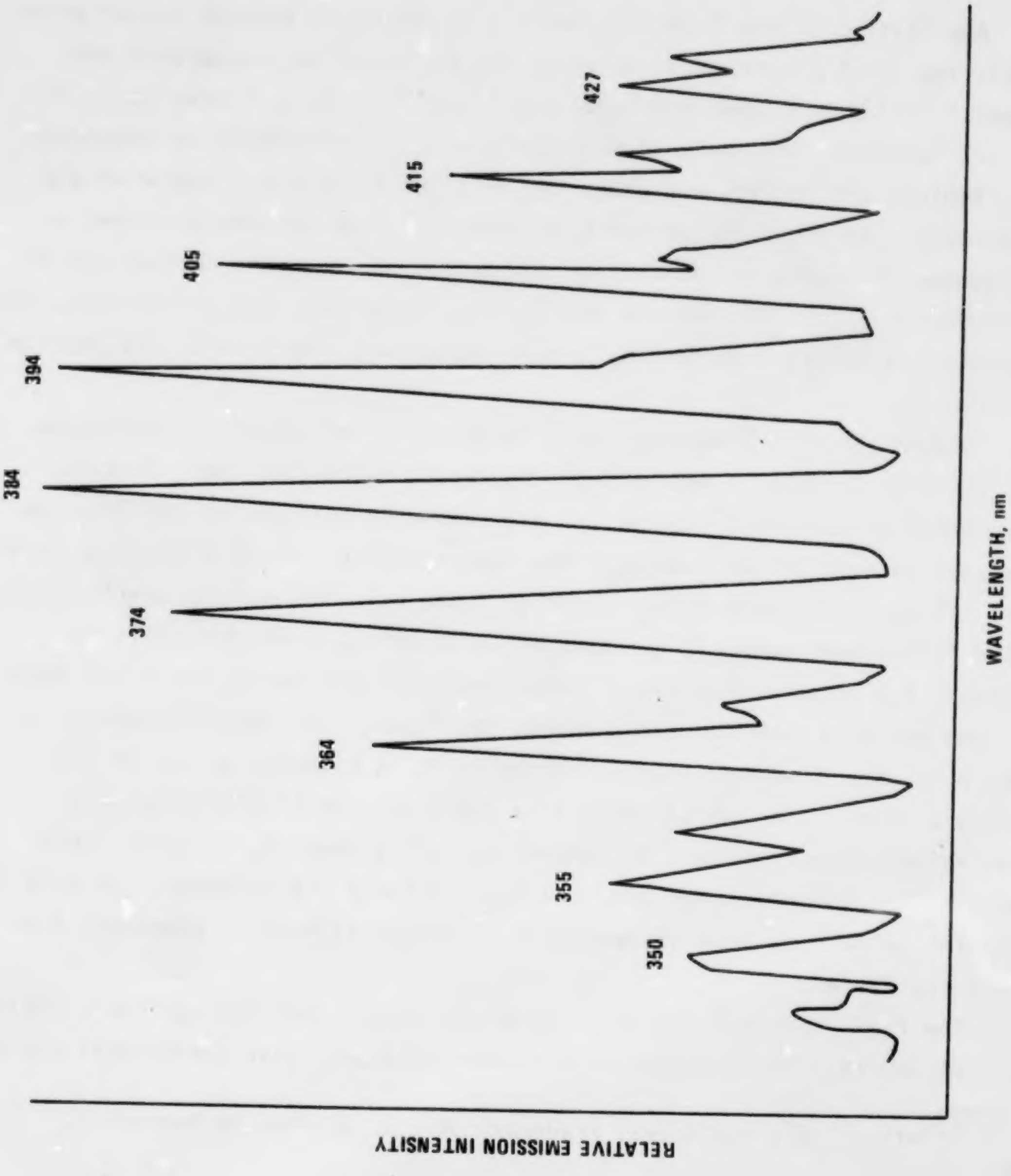

Figure 1.1. S_2 emission bands observed in a shielded air-hydrogen flame.

The exact theoretical exponential factor of 2 is not usually found. Instead, a lower value is found. This diminishment is caused by variation in flame conditions and by self-collisional quenching processes without chemiluminescence.

1.2 APPLICATION OF FPD TO CONTINUOUS DETECTION OF SO_2 IN AMBIENT AIR

1.2.1 Background: Principles of Operation

Application of the flame photometric technique to measure sulfur gases in air was first disclosed in a German patent issued to Draegerwerk and Drager.[8] Crider[9] in 1965 and Brody and Chaney[10] in 1966 further optimized the FPD technique for analysis of a variety of sulfur-containing compounds.

Ambient air FPD SO_2 analyzers are designed to supply a sample of air continuously to the flame photometric detector. The air sample serves as the source of oxygen to support the combustion of the hydrogen fuel and to maintain the flame. To achieve sensitivity, stability, and selectivity, the continuous analyzer must possess certain pneumatic, electronic, and physical features.[11]

Figure 1.2 illustrates the gas flow pathways of a typical continuous FPD analyzer for SO_2 in ambient air. A vented evacuation pump, located downstream of the burner, pulls the air sample or calibration gas into the analyzer through Teflon[†] tubing. The sample passes through a 5-micron pore size Teflon particulate filter (caution: use only the manufacturer's specified filter arrangement), a rotameter, a three-way solenoid valve, an optional H_2S scrubber assembly,[12] and finally enters the burner block where it combines with hydrogen and supports the flame. The sample rotameter is used only when flows are checked; normally it is bypassed by use of the solenoid valve. The H_2S scrubber is a required item on EPA-designated "equivalent method" units. It removes H_2S and allows SO_2 to pass. This improves the specificity of the analyzer. Without the scrubber, the unit is a "total sulfur" analyzer and responds to almost all sulfur compounds that reach the flame.

The fuel, hydrogen, enters through stainless steel tubing from a pressurized source. It first passes through a solenoid valve (which will close

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[†] "Teflon" is a registered trademark of E.I. Du Pont de Nemours & Co.

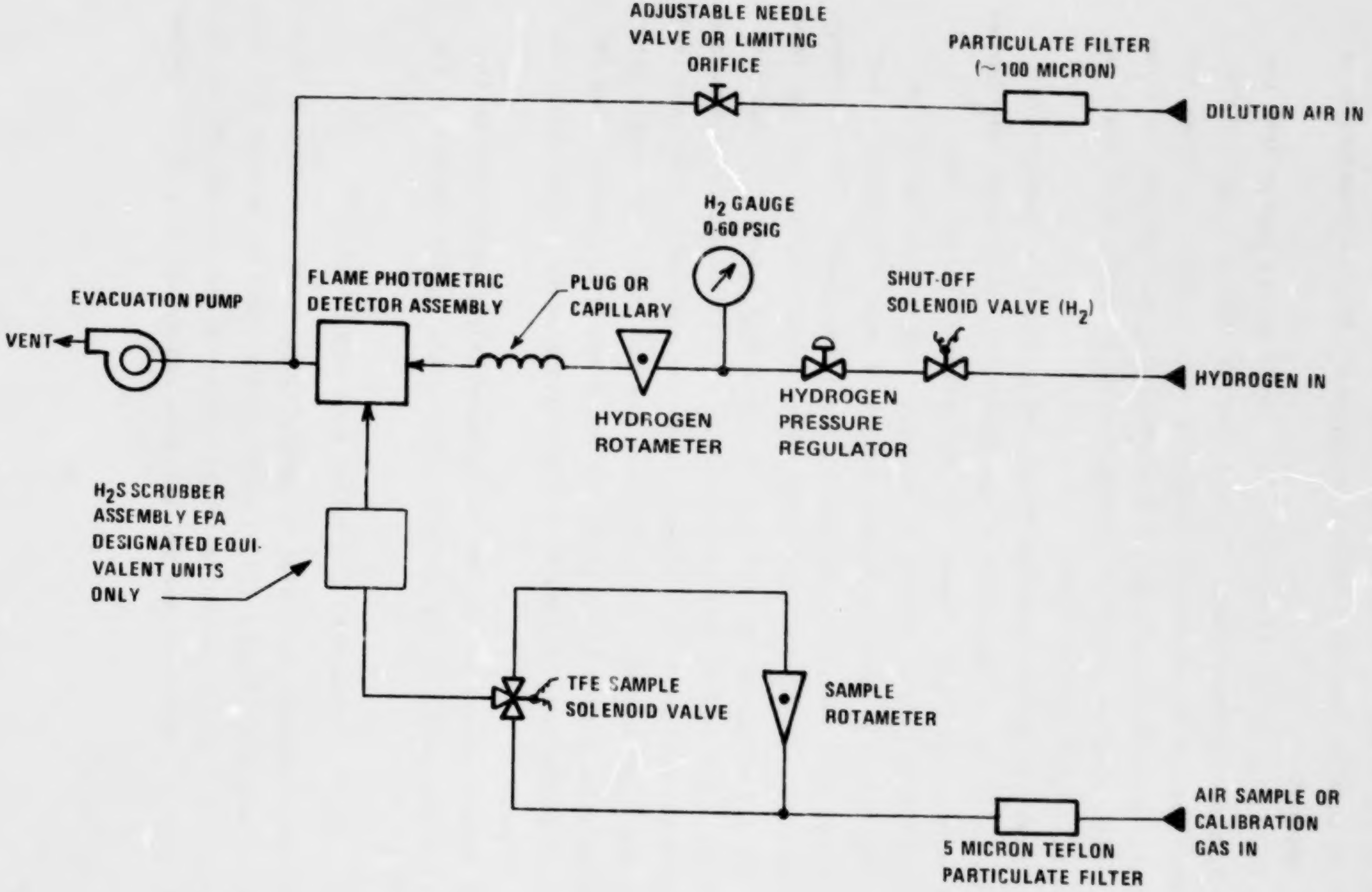
ADJUSTABLE NEEDLE VALVE OR LIMITING ORIFICE
PARTICULATE FILTER (~100 MICRON)
DILUTION AIR IN
H_2 GAUGE 0-60 PSIG
FLAME PHOTOMETRIC DETECTOR ASSEMBLY
EVACUATION PUMP
VENT
PLUG OR CAPILLARY
SHUT-OFF SOLENOID VALVE (H_2)
HYDROGEN IN
HYDROGEN ROTAMETER
HYDROGEN PRESSURE REGULATOR
H_2S SCRUBBER ASSEMBLY EPA DESIGNATED EQUIVALENT UNITS ONLY
TFE SAMPLE SOLENOID VALVE
SAMPLE ROTAMETER
AIR SAMPLE OR CALIBRATION GAS IN
5 MICRON TEFLON PARTICULATE FILTER

Figure 1.2. Gas flow diagram of continuous flame photometric detector for SO_2 in ambient air.

automatically if the flame should go out, thus preventing a hazardous buildup of hydrogen), then through a pressure regulator and gauge, through a flow-indicating rotameter, and then through a flow-limiting plug or capillary tube to the burner. To achieve a steady flow of hydrogen, the plug or capillary is usually located within an oven, where it is maintained at a constant temperature.

The third flow of gas is dilution air. Room air is pulled into the analyzer by the evacuation pump. It first passes through a particulate filter, then through an adjustable needle valve or limiting orifice, and finally meets and dilutes the vapors that are being pulled from the flame chamber. This dilution prevents condensation of unwanted water vapor and corrosive products from the flame.

The flame photometric detector itself is housed in a temperature-controlled cell. It is made up of three functional subsystems: the burner or flame holder, the flame chamber, and the photomultiplier tube. Air carrying sulfur-containing molecules enters through the bottom of the burner. The burner provides a support for the flame. The flame is surrounded by hydrogen, which is enclosed by the flame chamber. This arrangement produces a cool hydrogen-air flame, which is well-suited for the formation of the S_2* molecular species. It is a hydrogen hyperventilated diffusion flame. One wall of the flame chamber is a clear optical window and narrow bandpass optical filter through which the photomultiplier tube (PMT) measures the light emission intensity from the S_2* species at wavelengths near 394 nm and converts it to an equivalent electrical current. The PMT is temperature controlled. A regulated high-voltage power supply stabilizes the PMT output.

The output current of the PMT is approximately proportional to the square (the 2nd power) of the concentration of the sulfur present in the sample.[13]

$$\text{response} \simeq (\text{sulfur atom concentration})^2$$

The actual exponential value is generally somewhat less than 2, usually between 1.7 and 1.9. Figure 1.3 illustrates the chemiluminescent S_2* emission intensity - sulfur concentration relationship for the 400-380 nm (4,000-3,800 Å) region. Note that the PMT currents and sulfur dioxide concentra-

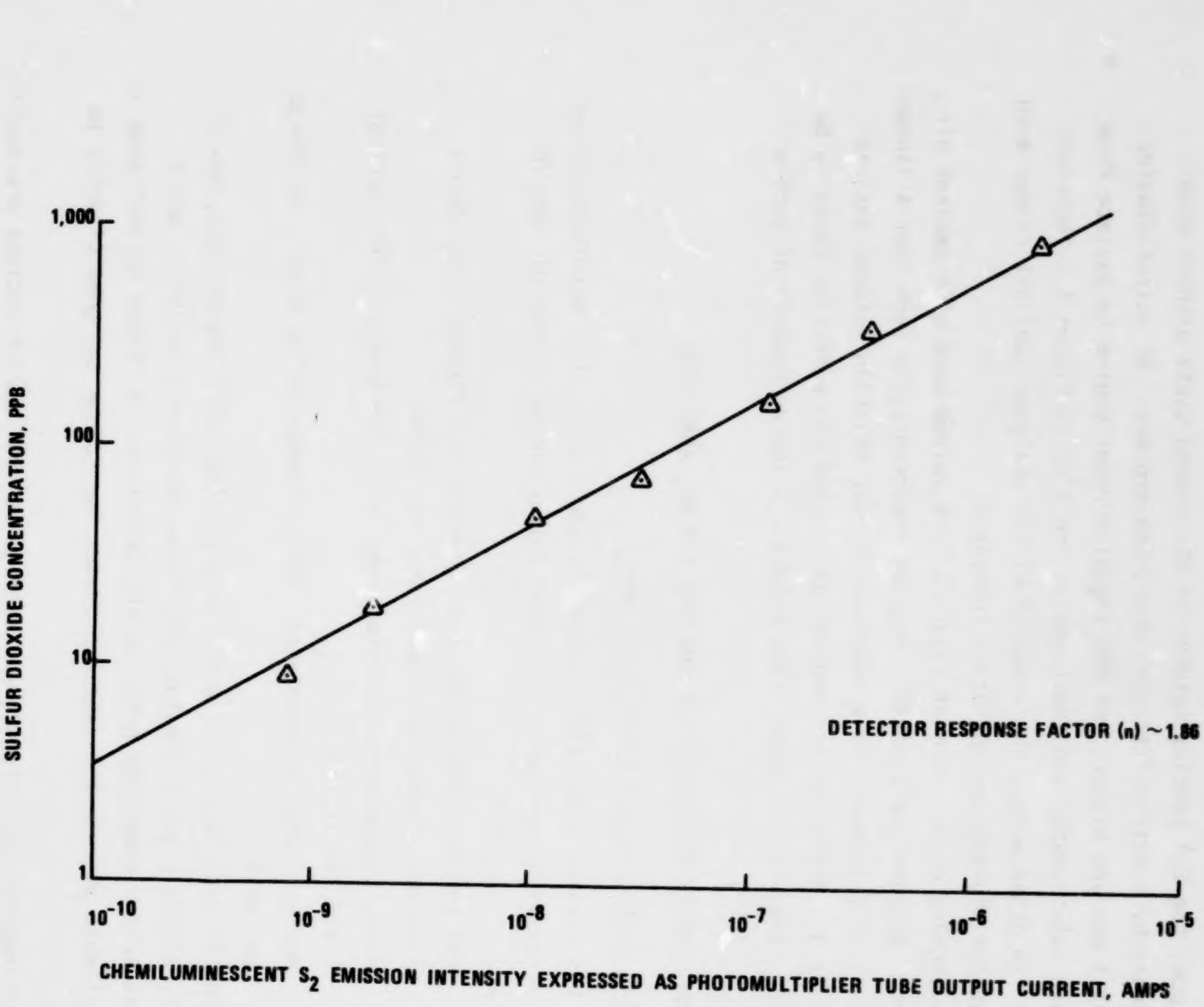

Figure 1.3. Flame photometric detector (FPD) sulfur response characteristics (Monitor Labs FPD).

tions are plotted on a log-log graph. Note that the slope of the line is 1.86, fairly near the theoretical slope of 2.00. Beyond concentrations of about 1 ppm, the S_2* species returns to its ground state without chemiluminescense by a self-collisional quenching process. At sulfur dioxide levels of 1 ppm and higher, the FPD signal current begins to deviate from the square relationship and the slope of the line in Figure 1.3 increases rapidly. In other words, the response of the analyzer does not change much as the sulfur dioxide concentration increases.

The log-log output form of Figure 1.3 is seldom used with ambient air analyzers. Instead the signal is treated electronically such that a linearized signal is obtained. This enables a linear relation between analyzer response (e.g., output volts) and sulfur dioxide concentration (ppm) to be plotted on linear graph paper. See Figure 4-3 for an example of such a plot.

1.3 COMMERCIALLY AVAILABLE FPD AMBIENT AIR SO_2 ANALYZERS

1.3.1 Manufacturers and Their Instruments

At the present time (1978) there are three major U.S. manufacturers of continuous-type FPD analyzers for total sulfur and/or sulfur dioxide in ambient air. These are:

1. The Bendix Corporation, Environmental and Process Instruments Division, Drawer 831, Lewisburg, WV 24901
2. Meloy Laboratories, Incorporated, 6715 Electronic Drive, Springfield, VA 22151
3. Monitor Labs, Incorporated, 4202 Sorrento Valley Blvd., San Diego, CA 92121

A fourth manufacturer, Tracor, Incorporated, 6500 Tracor Lane, Austin, TX 78721, offers a gas chromatography-flame photometry analyzer, which separates sulfur compounds prior to FPD detection. A "total sulfur" mode is also available wherein the sample bypasses the column and goes directly to the FPD.

Performance, operational, and configurational specifications are available from each manufacturer on a full line of FPD analyzers and options. Each of the manufacturers of continuous analyzers has one or more analyzers, which has been designated as an "equivalent method" by EPA or is a candidate for designation. This designation is discussed in Section 1.3.2. Such designation means only that the analyzer meets certain minimum standards. Competitive differences exist between FPD analyzers. Thus, the need for a careful selection process based on the individual air-monitoring situation is very important.

Indeed, if new SO_2 ambient air monitoring equipment is to be purchased, consideration should also be given to other methods of SO_2 detection that have been designated as equivalent methods or are candidates for designation. Such measurement methods include amperometric analyzers (Phillips Instruments, Incorporated), second derivative spectroscopy (Lear-Siegler Corporation), and pulsed UV fluorescence analysis (Thermo-Electron Corporation and Beckman Instrument Corporation).

1.3.2 Compliance Monitoring-Reference and Equivalent Methods

Certain air pollution control agencies, such as State agencies, are required to monitor the ambient air to determine compliance with National Ambient Air Quality Standards. The standards are given in Title 40, Chapter 1, Part 50 of the Code of Federal Regulations. Specific monitoring requirements are given in Part 51. An amendment to Part 51 was issued on February 18, 1975 (40 CFR 7043), and requires that for purposes of compliance monitoring "each method for measuring SO_2, CO, or photochemical oxidant . . . shall be a reference method or equivalent method . . . " An exception to this requirement allows automated analyzers purchased prior to February 18, 1976, to be used until February 18, 1980.

The definitions and qualifications of reference and equivalent methods are given in 40 CFR Part 53. For SO_2, the reference method is a manual method and is completely specified in Appendix A of 40 CFR Part 50. Thus, all other methods for SO_2 compliance measurement must be designated as equivalent methods by EPA. A notice of each method designated as equivalent is published in the Federal Register. A current list of all designated reference and equivalent methods is maintained by EPA and may be obtained from EPA Regional Offices or from the Environmental Monitoring and Support Laboratory, Department E, MD-76, Research Triangle Park, NC 27711.

Sellers of designated methods for sulfur dioxide must comply with certain conditions, one of which is that the analyzer must function within the limits of the performance specifications given in Table 1.1 for at least 1 year after delivery when maintained and operated in accordance with the operation manual. Aside from occasional breakdowns or malfunctions, consistent or repeated noncompliance with any of these specificatons should be reported to EPA at the address given previously.

For automated methods, a designation applies to any analyzer that is identical to the analyzer described in the designation. In many cases, analyzers manufactured prior to the designation may be upgraded (e.g., by minor modification or by substitution of a new operation or instruction manual) so as to be identical to the designated method and thus achieve designated status at a modest cost. The manufacturer should be consulted to determine the feasibility of such upgrading. Any modification to a reference or equivalent method made by a user must be approved by EPA if the designated status is to be maintained.

1.3.3 Recommendations for Use of Nonequivalent FPD Sulfur Analyzers

As was mentioned in the last section, older FPD analyzers may be upgraded and, thus, achieve designated status at modest cost. Any modifications should be done after consultation with the manufacturer and obtaining EPA approval.

This section contains recommendations for modifications and procedural changes to make older FPD sulfur analyzers more sensitive and more specific for SO_2. It must be emphasized that making these modifications yourself does not make your analyzer an equivalent method. However, for noncompliance monitoring and until such time as an equivalency-designated instrument is necessary, these steps should help give better data.

Replace all sampling lines. All sampling lines leading from the monitoring station ambient air manifold to the rear of the analyzer should be cleaned or replaced entirely with new cleaned Teflon tubing. This maintenance is necessary because the SO_2 in the sample can be adsorbed or reduced chemically be dirt, oil, and other debris on the tube wall. Frequency of tubing replacement should be determined by visual inspection of the line. Any fittings which are made of metal or plastic and come into contact with the sample should be either replaced with Teflon fittings or bored out so the Teflon tube passes continuously through the fitting. Tubing inside the

Table 1.1. Performance specifications for automated methods for SO_2[†]

Performance parameter	Units[‡]	Sulfur dioxide	Definitions and test procedures
1. Range	Parts per million	0-0.5	§53.23(a).
2. Noise	do	0.005	§53.23(b).
3. Lower detectable limit	do	0.01	§53.23(c).
4. Interference Equivalent			§53.23(d).
Each interferent	do	±0.02	
Total interferent	do	0.06	
5. Zero drift, 12 & 24 hr	do	±0.02	§53.23(e).
6. Span drift, 24 hours			
20% of upper range limit	Percent	±20.0	§53.23(e).
80% of upper range limit	do	± 5.0	§53.23(e).
7. Lag time	Minutes	20	§53.23(e).
8. Rise time	do	15	§53.23(e).
9. Fall time	do	15	§53.23(e).
10. Precision			§53.23(e).
20% of upper range limit	Parts per million	0.01	
80% of upper range limit	do	0.015	

[†] Table 1.1 is reproduced from a portion of Table B-1 of CFR 40 Part 53.

[‡] To convert from parts per million to micrograms per cubic meter at 25° C and 760 mm Hg, multiply by M/0.02447, where M is the molecular weight of the gas: $M = 64$ for SO_2

analyzer that leads to air flow rotameters and to the burner block should also be removed and replaced. The sample should not pass through the rotameter during normal sample monitoring operations since SO_2 gas is removed by the rotameter components; it should bypass the rotameter. Any solenoid valves which are in the sample line should have Teflon interiors and should be cleaned or replaced if dirty. A Teflon holder with membrane filter, such as the "Mace" filter (available from the Mace Corporation, S. El Monte, CA 91733), mounted in the sampling line will minimize particulate accumulation.

Clean burner block and "window." The burner block of most FPD analyzers can be removed and disassembled. Accumulated dust and corrosion are removed (use fine steel wool) and the surfaces and fittings are cleaned with mild soap and water. It is advisable to replace any "O" rings with new ones at this time. Use only the manufacturer's recommended "O" rings since others may tend to cold-flow or otherwise lose their sealing properties. For example, the Meloy model SA-285 requires Viton "O" rings. Next, rinse the parts with deionized water and then allow them to dry. It may be necessary to replace the thermocouple sensor and the ignitor wire or glowplug at this time. If the thermocouple is removed or replaced, be sure it is re-installed identically to the original thermocouple. If the polarity of the leads is reversed, the circuitry controlling the H_2 solenoid may actuate and stop the hydrogen flow, giving a flame-out. Also check the operability of burner block heating elements and replace them if necessary. Between the flame and the photomultiplier tube are a clear "window" and a 394 ± 20 nm optical filter. Examine each for cloudiness, staining, or pitting, and clean or replace them as necessary. This will allow more light to reach the PM tube. Some manufacturers suggest that the burner block be flushed with certain solvents and then dried. This procedure is outlined in the manufacturer's instruction manual and may be used.

Overhaul or replace sample pump. If the analyzer contains a pump, it is probably a small bellows pump or diaphragm pump. Over long periods of use, these pumps develop problems in the diaphragm area (due to dust and general fatigue), and variable flows result. Replace any worn parts and reseal the pump properly. A new valve assembly may be required for bellows pumps. Consult the pump manufacturer's maintenance instructions regarding allowable vacuum pressure and flow rate limits. If an external pump is used, be sure it is of sufficient capacity to do the job and that it operates smoothly.

Install filter on dilution air entry. Older models may not have particulate filters on the dilution air entry at the rear of the analyzer. To minimize particle and dust entrainment, which might alter the dilution flow rate, install a simple in-line filter. The filter should pass air easily so that adequate flow is maintained. Porous paper filters mounted in small plastic holders work well.

Install H_2S scrubber. The H_2S scrubber is an item which seldom accompanied older FPD analyzers since they were designed as "total sulfur" monitors. Today, each of the three major FPD analyzer manufacturers provides separate H_2S scrubbers, which can be purchased and installed on older analyzers. These scrubbers remove H_2S but allow SO_2 to pass unaffected.

Clean or replace and recalibrate rotameters. Most analyzers have hydrogen fuel and air sample rotameters to indicate flow rates. After long usage, these rotameters may become dirty and dusty and require disassembly and cleaning. Methanol is suggested as a cleaning solvent. Use it in a ventilated area since methanol is toxic. After drying and reassembly, the rotameter should be calibrated (or the certified calibration curve, which accompanied the rotameter, should be verified) by comparison to a certified soap film flowmeter, spirometer, or wet test meter. For normal ambient air monitoring, the air sample should bypass the rotameter and flow directly to the flame compartment.

Electronic checks. If there is reason to suspect that the electronics need repair or coarse adjustment, a qualified electronic technician or service representative should examine and test the analyzer. Adjustments may be made prior to the calibration procedure.

Calibration procedure. Some users of older FPD analyzers may be accustomed to calibrating an analyzer by simply "zeroing" and "spanning" the analyzer. This practice is discouraged.

To operate an analyzer designated as an "equivalent method," a more detailed monthly calibration, which includes a zero point, span point, and three or more intermediate concentration points, is initially recommended. If possible, one or more of the calibration points should be representative of the concentration levels that are actually being experienced in the ambient air. Use of multiple calibration points shows the linearity (or lack of linearity) of the analyzer's response. A lack of linearity can be corrected by adjustment of the linearization circuitry as specified by the manufacturer. The use of graphical display of calibration data and least squares regression equation computations are suggested. Details for carrying out such a calibration are given in Section 4.0 of this document.

1.4 CALIBRATION GAS DELIVERY SYSTEM: SOURCES OF SO_2

A reliable and accurate system of delivering known concentrations of SO_2 calibration gas to the FPD analyzer is a necessity. Several commercial systems are available. They usually employ permeation tubes or devices as SO_2 sources. The temperature of the tube or device is controlled by use of a thermostatted water or air bath or other method. Calibrators may also be fabricated by the user. Desirable characteristics of dynamic SO_2 calibrators and general instructions for their use are given in Section 3.0 of this document.

The source of SO_2 should be an NBS-certified permeation tube or another tube or device whose permeation rate is traceable to an NBS Standard Reference Material tube. Sources of air for dilution of permeation tube effluent are also discussed in Section 3.0. Particular attention should be given to both the CO_2 and O_2 content of diluent air. The use of SO_2 in air from compressed gas cylinders is also discussed in Section 3.0.

1.5 RECORDKEEPING, MAINTENANCE, AND QUALITY CONTROL

Proper recording of all data from calibrations, zero and span checks, etc., is essential to overall data quality. This document does not give a format for data recording, but does emphasize when data should be recorded.

Preventive maintenance and major maintenance items are only noted in this document. The user should refer to the analyzer's instruction manual for details of maintenance and troubleshooting procedures.

Quality control and quality assurance are most important to insure production of good data. A major aspect of quality control is calibration. This is treated thoroughly in this document. For other aspects of quality control and assurance, the reader is referred to the EPA publications "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles" (EPA-600/9-76-005, March, 1976) and "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods" (EPA-600/4-77-027a, May, 1977).

SECTION 2.0

INSTALLATION AND STARTUP OF THE FPD SO_2 ANALYZER

2.1 INTRODUCTION

Correct installation and startup of an FPD SO_2 analyzer is the first step of an ambient air monitoring program for SO_2. In addition to a well-equipped tool box, brass, stainless steel and Teflon tubing, compression fittings, signal cable, hydrogen fuel, and a hydrogen regulator will be required. Flow-measuring devices such as a selection of rotameters and a soap film flowmeter are necessary. A wet test meter and a mass flowmeter are useful, especially in the laboratory. A stopwatch, hand calculator, and a recorder or digital voltmeter will also be required.

If the analyzer is to be installed and used in a laboratory, the necessary equipment for calibration, etc., will generally be available. If the analyzer is to be installed at a field station (unattended operation), it is recommended that the analyzer first be unpacked, checked, set up, calibrated, and operated for several days at the central laboratory. This procedure will contribute to better understanding of the analyzer and will demonstrate its proper calibration and operation before field usage. The analyzer is then taken to the field site, installed, and calibrated.

VERY IMPORTANT: before beginning any installation procedures, first read the manufacturer's operation and maintenance manual for your FPD analyzer. Become familiar with the location and function of all controls and gas and electrical connections. If the original manual is lost or misplaced, order a replacement.

2.2 REQUIREMENTS OF THE FACILITY WHICH HOUSES THE ANALYZER

The room, trailer, or shelter which houses the analyzer will probably also house other ambient air monitors, calibration systems, meteorological systems, strip chart recorders, and perhaps a magnetic tape data acquisition system.

The physical facility housing the FPD analyzer should meet certain requirements so that optimum analyzer performance is obtained.

2.2.1 Electrical Requirements

> Note: before connecting any power to your FPD analyzer, be certain that all switches for power, pump, etc., are in the OFF position. Unusual power surges have been known to cause damage to photomultiplier tubes and other analyzer components.

Commercial instruments operate over the voltage range 105-125 on 60 Hz, single phase power. Be sure there are no voltage fluctuations in the line. If such fluctuations are suspected, the power company can detect and perhaps correct the problem. Power requirements vary from 250 to 500 W. For reasons of safety (prevention of electrical shock), proper operation of the analyzer, and warranty requirements, it is essential that adequate power be present for the monitoring site and that power be supplied to the analyzer through the conventionally grounded 3-pin power plug supplied with the analyzer. This ground must not be defeated by cutting off the round pin on the power cable. If the instrument must be operated from the two-contact outlet, grounding is preserved by using a three-conductor to two-conductor adapter and connecting tne adapter wire to a suitable ground such as a cold water pipe or a grounding rod (embedded in soil). The use of extension cords is not recommended unless they are of the heavy duty type.

2.2.2 Temperature and Humidity Control Requirements

Each of the commercially available instruments is designed to operate (with minimal effect on instrument drift) over the temperature range 20° - 30° C (74° - 86° F) and over the range 10° - 40° C with possibly significant degradation in the noise, precision, and drift specifications.

Other ambient air monitors will have similar temperature range requirements. The best environment is an air-conditioned/heated room with a thermostat that maintains the room temperature somewhere in the range 20° - 30° C. A temperature of 25° C (77° F) is ideal since this is the "standard" temperature for air sampling. If the instrument is rack-mounted, it is important that the rack enclosure be properly ventilated. The temperature inside enclosed relay racks which are not ventilated may be as much as 15° - 25° C above laboratory ambient temperatures.

One must be careful not to let the temperature inside the laboratory or sampling site facility fall too low, as this can cause water from the moist ambient air to condense in the station air sampling manifold and possibly condense in the sampling lines leading to the instruments. This will cause removal of SO_2. Deflect the cold air from air conditioners or relocate the air conditioner away from the manifolds and sampling lines. If condensation problems persist, it may be necessary to insulate and slightly heat the station sampling manifold and instrument sampling line.

All of the above variations in temperature may cause the instrument to respond in an erratic, drifting, manner, due to temperature changes across the burner block assembly.

Another note on temperature effects concerns the exhaust or vent line from the flame photometric detector. Since hydrogen is being burned in the flame chamber, water is produced and exhausted from the instrument. Dilution air mixes with the water-laden hot exhaust gases to reduce the amount of water per volume of air to a point below the dew point at normal room temperatures. If the temperature of the facility is low enough to cause condensation of this water, a "plug" of water may form in the vent line. This will cause the sample flow of the analyzer to vary since both dilution air and sample air are pulled in with the same pump and disturbance of one flow affects the other. To avoid this, a 6.4 mm (0.25 in.) o.d. exhaust line (polyethylene is acceptable) should be installed in such a way that drainage of water always occurs and no points exist where water can stand in the line.

The exhaust line should be vented to a point outside the building or to a vent system whose ultimate exit is well away from the sample inlet source and occupied enclosed areas. In this way excess hydrogen will be safely vented to the ambient air if the instrument's flame is extinguished and the instrument has no hydrogen solenoid shutoff or the solenoid fails. The length of the exhaust line should be minimal. If the length is changed it should be done just prior to a multipoint calibration. If the exhaust line leads to the outside ambient air, proper drainage should be maintained outside, too. Extremely cold weather may cause condensation and freezing of water in the line with subsequent disruption or change of air flows. The tube may be insulated by covering it with plastic tubing having an inside diameter slightly larger than the outside diameter of the exhaust tube.

2.2.3 Spatial Requirements

Adequate space should be allotted for analyzer operation and calibration. If the instrument (or instrument modules) is rack-mounted, there should be sufficient space around the rack to allow free circulation of air to provide good heat dissipation. The bench mount configuration is quite handy as it allows convenient access to the interior of the analyzer for maintenance and adjustment.

In either case, sufficient room should be available adjacent to the analyzer to locate a sulfur calibration source and associated equipment such as bubble flowmeters and mass flowmeters. It is a good idea, if space permits, to have easy access to the rear panel of the analyzer so that electrical and pneumatic lines and in-line filters and scrubbers can be easily checked or changed.

2.2.4 Ambient Air Sampling Requirements

Air should be brought into the sampling station through an ambient air sampling manifold of glass or Teflon construction. A 60-100 cfm (free air) blower motor is located at one end to pull the air sample into the station at the rate of several cubic feet per minute and exhaust the excess air to the outside. The blower motor should be easily accessible for periodic checks of its proper operation. The glassware of the manifold itself should be disassembled and cleaned from time to time, especially when dust and dirt buildup becomes noticeable. Clean it with warm water and rinse with deionized water. The Teflon sampling line of the analyzer is connected to the manifold. Figure 2.1 illustrates several ways to make this connection. Whatever way is used, it should be compatible with both the ambient air and calibration manifolds. Air inlets of calibration systems which "manufacture" zero air for use with permeation tubes or other calibration gas sources are also connected to the sampling manifold. In this way, ambient

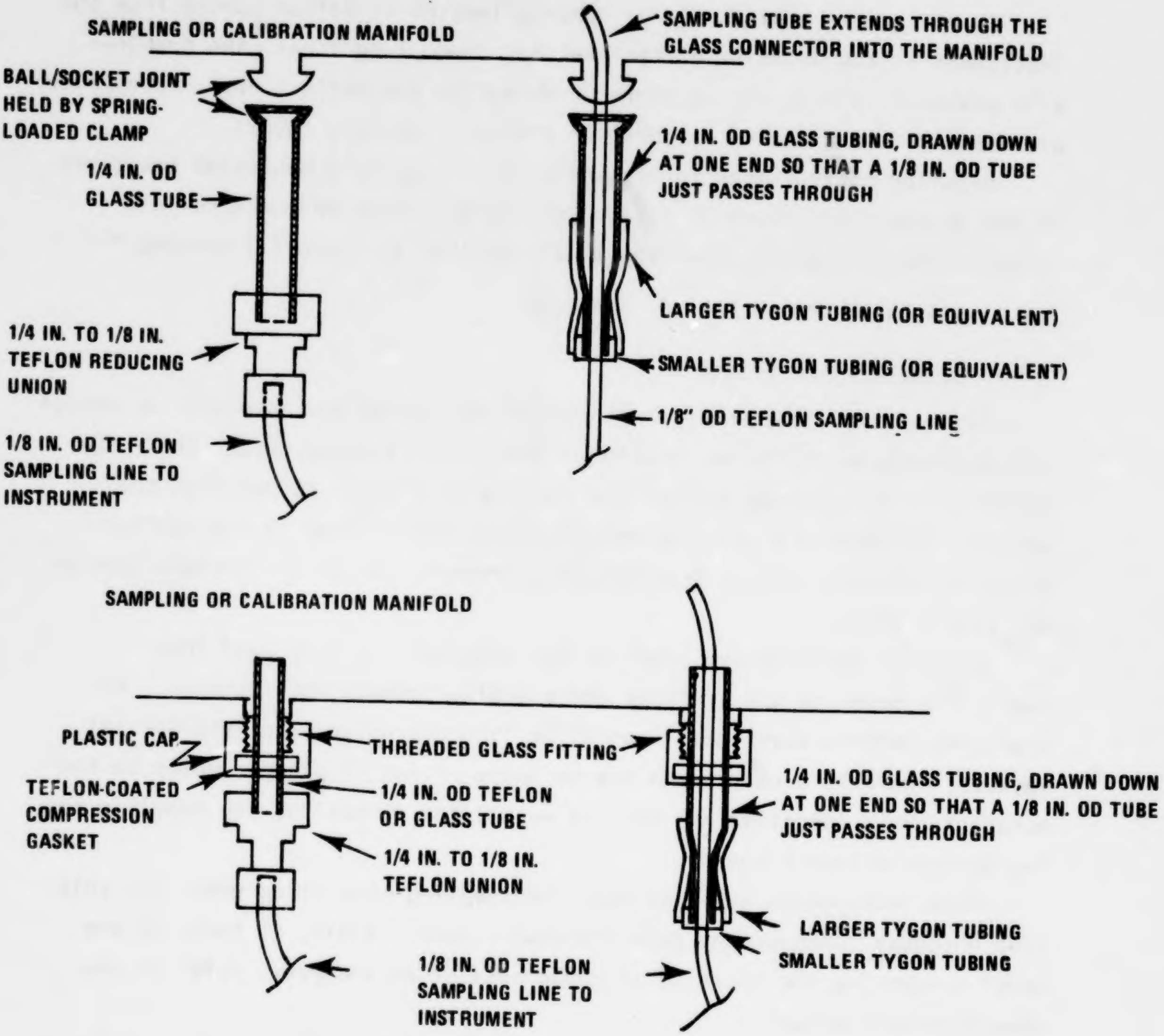
SAMPLING OR CALIBRATION MANIFOLD
BALL/SOCKET JOINT HELD BY SPRING-LOADED CLAMP
1/4 IN. OD GLASS TUBE
1/4 IN. TO 1/8 IN. TEFLON REDUCING UNION
1/8 IN. OD TEFLON SAMPLING LINE TO INSTRUMENT
SAMPLING TUBE EXTENDS THROUGH THE GLASS CONNECTOR INTO THE MANIFOLD
1/4 IN. OD GLASS TUBING, DRAWN DOWN AT ONE END SO THAT A 1/8 IN. OD TUBE JUST PASSES THROUGH
LARGER TYGON TUBING (OR EQUIVALENT)
SMALLER TYGON TUBING (OR EQUIVALENT)
1/8" OD TEFLON SAMPLING LINE
SAMPLING OR CALIBRATION MANIFOLD
PLASTIC CAP
TEFLON-COATED COMPRESSION GASKET
THREADED GLASS FITTING
1/4 IN. OD TEFLON OR GLASS TUBE
1/4 IN. TO 1/8 IN. TEFLON UNION
1/8 IN. OD TEFLON SAMPLING LINE TO INSTRUMENT
1/4 IN. OD GLASS TUBING, DRAWN DOWN AT ONE END SO THAT A 1/8 IN. OD TUBE JUST PASSES THROUGH
LARGER TYGON TUBING
SMALLER TYGON TUBING

Figure 2.1. Detailed views of various ways for connecting 1/8 in. o.d. Teflon sampling lines to manifold.

levels of carbon dioxide (CO_2) are supplied to the instrument. Refer to Section 3.0 for a discussion of the CO_2 effect on FPD analyzers.

Do not sample ambient air by running lengths of Teflon tubing from the instrument to the exterior of the station. Such long lines give problems with pressure balance and moisture condensation and collect dust. They also are awkward to use during calibration and zero and span checks.

Detailed instructions for installation of sampling manifolds are given in EPA document EPA-600/4-77-027a, "Quality Assurance Handbook for Air Pollution Measurement Systems-Volume II, Ambient Air Specific Methods."

2.3 INSTALLATION OF AN FPD SO_2 ANALYZER

2.3.1 Unpacking the Analyzer

Upon receipt, the analyzer should be unpackaged and examined for damage such as scratched surfaces, broken or bent control knobs, etc. Check the contents of the package against the packing slip which accompanies the parcel. If there are shipping deficiencies, report them to the manufacturer; if there is damage from shipping, report this to the freight carrier and file a claim.

Prior to applying any power to the analyzer, it is a good idea to remove the cover of the analyzer and visually inspect the interior. All analyzers contain electronic "cards" or "boards" which plug into special sockets; there is a chance one may be loose or not in place. Refer to the manufacturer's operation and service manual for directions for handling and replacing electronic boards.

Some instruments may also have the sampling pump "tied-down" for shipping purposes. Remove any such tie-down straps. Again, if there is any doubt concerning the location of components of an analyzer, refer to the manufacturer's manual.

Save the shipping box or crate in the event the analyzer may have to be returned to the manufacturer or be moved to another site.

2.3.2 Electrical and Pneumatic Connections

Electrical and pneumatic (gas) connecting terminals are located on the rear panel of most FPD SO_2 analyzers. Figure 2.2 illustrates a typical installation.

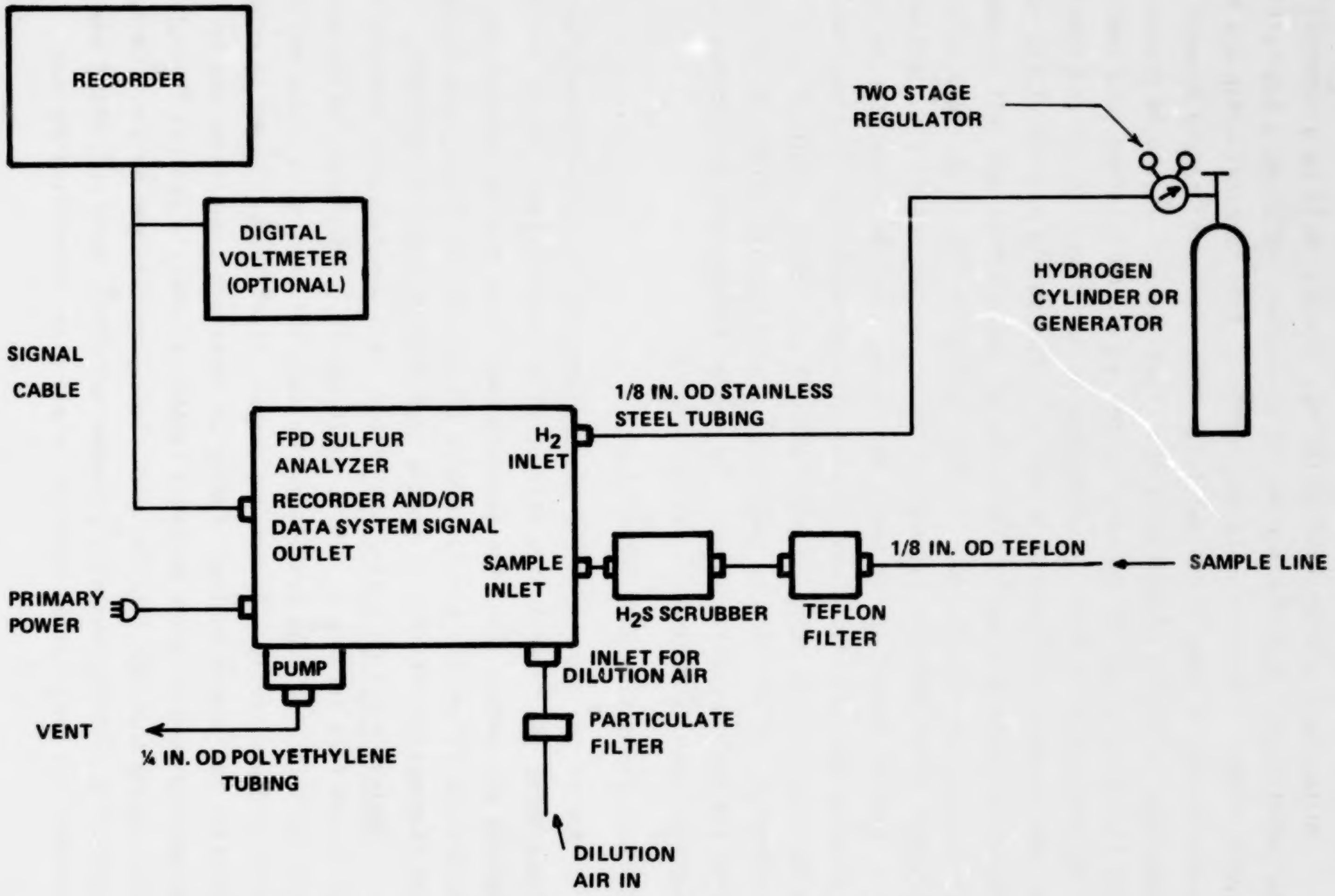
RECORDER
TWO STAGE REGULATOR
DIGITAL VOLTMETER (OPTIONAL)
HYDROGEN CYLINDER OR GENERATOR
SIGNAL CABLE
1/8 IN. OD STAINLESS STEEL TUBING
FPD SULFUR ANALYZER
H_2 INLET
RECORDER AND/OR DATA SYSTEM SIGNAL OUTLET
1/8 IN. OD TEFLON
SAMPLE LINE
SAMPLE INLET
PRIMARY POWER
H_2S SCRUBBER
TEFLON FILTER
PUMP
INLET FOR DILUTION AIR
VENT
PARTICULATE FILTER
¼ IN. OD POLYETHYLENE TUBING
DILUTION AIR IN

Figure 2.2. Typical installation of FPD SO_2 analyzer.

2.3.2.1 Electrical Connections

On the rear of each kind of FPD SO_2 analyzer will be a terminal strip for electrical output connections to a recorder and/or data acquisition system (DAS). Connections to the screws on this terminal strip are best made with no. 6 spade lugs (available from electrical supply houses) which have been carefully connected to the signal cable. The cable interconnecting the analyzer to the recorder or DAS should be shielded twin lead wire (commonly called control, instrumentation, or signal cable) and should be of minimal length, less than 15 m (50 ft). The shield portion of the cable should be connected to the signal low at the analyzer and left unconnected at the recorder or DAS end. If the recorder or DAS is equipped with a guarded input, refer to its manual for proper interconnection instructions.

Special connectors or plugs may be required for connection to the recording device. Avoid any sort of wire splicing that involves twisting wires together and wrapping with tape. A continuous length of wire is preferred. If splicing is necessary, a good quality soldering job should be done and the wire reinsulated. The use of the mechanical compression connectors, such as "sta-kons," is acceptable.

2.3.2.2 Pneumatic (Gas) Connections

Any of the commercial FPD SO_2 analyzers will require connection of at least three gas lines to the rear panel of the analyzer. These are the ambient air sample line, the hydrogen fuel line, and the exhaust gas line. Be sure to follow the manufacturer's directions for use of tube connectors and compression fittings so that a leak-free assembly is obtained.

Ambient air sample line and filter. All manufacturers specify the use of 3.2 mm (1/8 in.) o.d. x 0.76 mm (0.030 in.) thick wall Teflon tubing. A roll of this should be available. Be sure this tubing is clean and has not been used previously. Do not use copper, steel, polyethylene or other plastics for sample tubing! Tubing of uncertain cleanliness may be cleaned by passing reagent grade methanol (methyl alcohol, a poison) through it and then drying the tube interior with clean, dry nitrogen or air. Certain tube connecting fitting (Swagelok®, Parker-Hannifin®, Gyrolok®, etc.) may be needed. Use only Teflon fittings or all-glass connecting devices.

The length of the sampling tube should not be excessive. Usually a length of 1.5 m (4 to 6 ft) is ample to reach the station sampling manifold. Use this line for both sampling and calibration.

It is recommended that an all-Teflon particulate filter be installed in the instrument sampling line. The filter should be a Teflon membrane with 5 μ or less pore size. Its holder should be constructed from a solid piece of Teflon or metal which is completely lined with Teflon. A suggested model is the Mace filter holder, series 930 (available from the Mace Corporation, S. El Monte, CA 91733) used in conjunction with 5 μ Teflon membrane filters, catalog no. 425-0001 (see Figure 4.1). Use of non-Teflon filters can destroy the SO_2 sample and may cause pressure problems in the analyzer's pneumatic system. Consult the manufacturer for his specific recommendations. The membrane filter should be replaced at the time of calibration, or more often if the instrument is located in a particularly dirty environment.

Exhaust gas line. The instrument's exhaust line should be 6.3 mm (1/4 in.) or greater o.d. polyethylene tubing. Since moisture may accumulate in this line, be sure it is installed in such a way that drainage will always occur. In some older FPD models, the exhaust line is connected to an external pump which has its own exhaust line. Any exhaust lines should be of the minimum length required to exhaust gases from the station.

Hydrogen fuel line. It is recommended for safety reasons that connection of the hydrogen supply (from a compressed gas cylinder or an electrolytic hydrogen generator) to the analyzer be made only through clean, dry stainless steel tubing. The tubing should be 3.2 mm (1/8 in.) o.d. Use stainless steel fittings. The hydrogen, if supplied from a cylinder, should be of "prepurified" grade or an equivalent or better grade. Percent purity is 99.95 or better.

The regulator used with the compressed hydrogen cylinder should be a two-stage metal diaphragm brass regulator with a delivery pressure range between 0 and 150 psig and should be equipped with CGA no. 350 cylinder valve outlet. This regulator must be free of sulfur-containing materials in its construction. Brass, stainless steel, and Kel-F or Teflon are suitable materials for internal construction. This regulator should be dedicated to use with H_2. A shut-off valve should also be included. A very important safety consideration would be the installation of a flow-limiting orifice near the regulator to limit the flow in case a leak or rupture occurs. A hydrogen regulator assembly is shown in Figure 2.3.

Observe the following safety requirements in the handling and use of hydrogen since it is an explosive material.

2.3.3 Guidelines for the Safe Use of Hydrogen Cylinders

Hydrogen is a highly flammable gas which is colorless, odorless, and tasteless. It burns in air with a flame that is almost invisible. Its chemical formula is H_2, its molecular weight is 2.016, and it is flammable in the 4 to 75% (by volume) range in air. A temperature of 585° C (1,085° F) is required for auto-ignition in mixtures of air or oxygen at atmospheric pressure. A spark can of course cause ignition at ambient temperatures. Electrical relays, contact closures, etc. are causes of sparks.

Precautions for handling and storing of hydrogen cylinders

The major hazard associated with the handling of hydrogen is its flammability. Be certain to follow these rules when handling hydrogen cylinders:

1. Never use cylinders of hydrogen in areas where flames, excessive heat, or sparks may occur.
2. Utilize only explosion-proof equipment, and spark-proof tools in areas where hydrogen is handled.
3. Ground all equipment and lines used with hydrogen.
4. Never use a flame to detect hydrogen leaks--use water or a commercial liquid leak detector such as "SNOOP®."
5. Do not store reserve stocks of hydrogen with cylinders containing oxygen or other highly oxidizing or combustible materials.

Precautions for H_2 cylinder use with FPD analyzers

1. Never move a hydrogen cylinder unless the regulator is removed and the cylinder cap is in position. Use a cylinder cart and chain the tank to it. Gloves and safety glasses or full face shield should be worn when moving tanks.
2. Do not expose the H_2 tank to mechanical stress by dropping it to the ground or dropping it from truck tailgates.

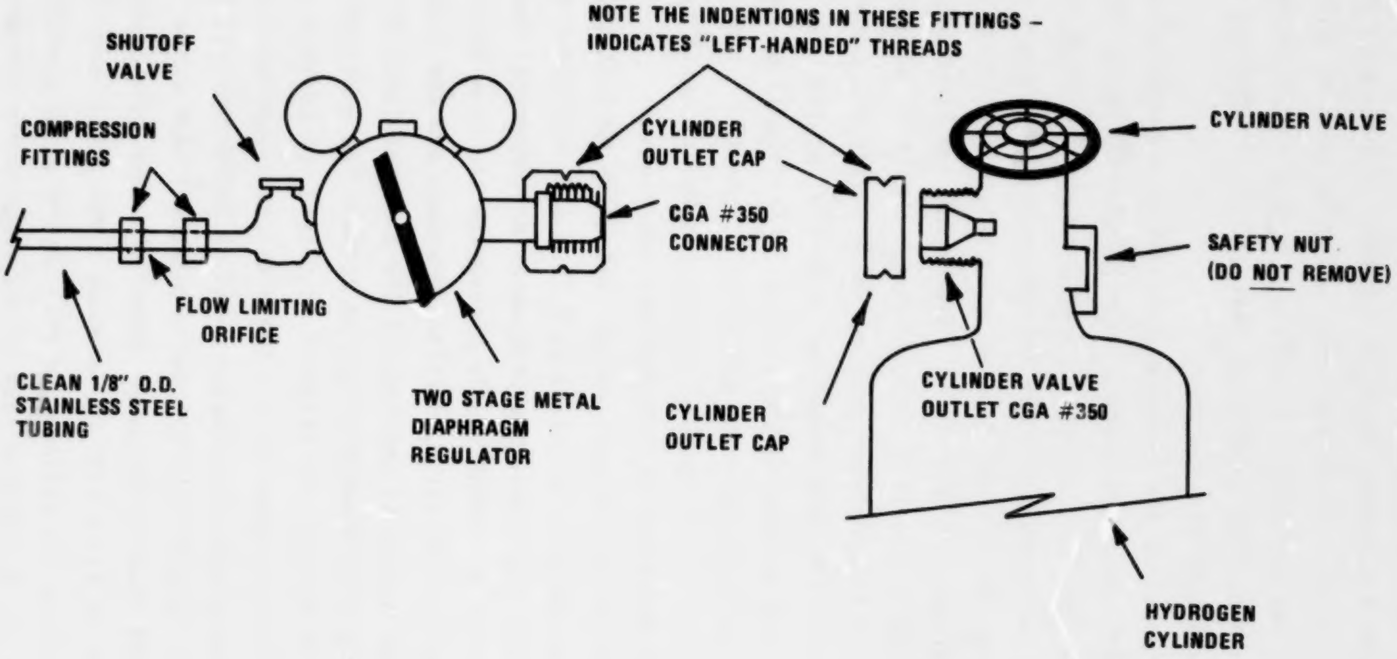
NOTE THE INDENTIONS IN THESE FITTINGS –
INDICATES "LEFT-HANDED" THREADS
SHUTOFF VALVE
COMPRESSION FITTINGS
CYLINDER OUTLET CAP
CYLINDER VALVE
CGA #350 CONNECTOR
SAFETY NUT (DO NOT REMOVE)
FLOW LIMITING ORIFICE
CLEAN 1/8" O.D. STAINLESS STEEL TUBING
TWO STAGE METAL DIAPHRAGM REGULATOR
CYLINDER OUTLET CAP
CYLINDER VALVE OUTLET CGA #350
HYDROGEN CYLINDER

Figure 2.3. Hydrogen regulator assembly and CGA cylinder connecter #350.

3. Locate the hydrogen cylinder in a well-ventilated area. If this is inside a building, be sure the tank is separated from nearby oxygen- or air-containing tanks. The H_2 tank may also be located outside the building. If outside, keep the tank protected from the weather, from sources of heat, flame, or sparks, and separate from oxygen or air cylinders.
4. Properly secure the hydrogen cylinder to a permanent or semi-permanent structure (such as a railing attached to the wall studs or to a laboratory benchtop) using a cylinder clamp with strap or chain. Be certain to have the cylinder properly secured before removing the cylinder cap and attaching a regulator.
5. The hydrogen cylinder and all equipment and lines associated with it should be electrically grounded. The three-wire grounding system of the analyzer grounds the analyzer and connections.
6. Never open the tank output valve or the regulator valve before connection is made to the analyzer. Self-ignition (auto-ignition) of the escaping hydrogen may occur. When the cylinder valve is open, open it all the way (counterclockwise) until turning stops. Leakage may occur at intermediate positions.
7. Connect the H_2 cylinder to the fuel entry port at the rear of the analyzer using only 3.2 mm (1/8 in.) o.d. stainless steel lines. Leak test the lines only with water or commercial leak check solutions such as "SNOOP®." To pressurize the line for a leak test: (a) verify that all connections are made and are tight from the cylinder outlet to the rear of the analyzer (test by snugging the fittings with wrenches); (b) be certain the analyzer is off so that the H_2-shut-off solenoid is closed, be certain the hydrogen regulator is closed (i.e., the pressure-adjusting knob or handle is rotated counterclockwise until it moves freely); (c) quickly open or "crack" the cylinder regulator's main valve, watch the pressure rise in the gauge nearer the tank (the pressure in a new H_2 tank at 21° C (70° F) is about 2,200 psig), and then immediately close the cylinder valve. If the gauge pressure decays as you watch, there is a leak in the regulator's connection to the cylinder or a leak through the regulator. If no leaks are indi-

cated, the pressure on the second gauge should be set to some point (say, 40 psig or the FPD analyzer's suggested setting). This will pressurize the line up to the instrument H_2 shutoff solenoid. Any major leaks will be indicated by a rapid decay of pressure in the regulator gauge. Check for small leaks by applying leak-detector solution around each connection and watching for small bubbles to form as the hydrogen escapes.

8. Never loosen or disconnect any hydrogen fitting or connector while the hydrogen is under pressure. Always cut the hydrogen off at the tank and allow the system to "bleed" down to ambient pressure.
9. In the event a major leak occurs while the hydrogen is under pressure, turn off the cylinder valve if possible and leave the station. Leave the door open for ventilation. Cut off electrical power at the breaker box outside the station.
10. When connecting the regulator to the cylinder, do not confuse the cylinder safety nut with the metal outlet cap which is frequently installed on the cylinder outlet. The safety nut connects directly to the valve inlet and once it is removed, the flow of gas cannot be stopped. Refer to Figure 2.3.

2.3.4 Procedures and Safety Precautions for Use of Electrolytic Hydrogen Generators

Electrochemical hydrogen generators produce hydrogen (H_2) (and oxygen (O_2)), by electrolysis of water. As with any hydrogen supply, one must be cautious in the use of the generator. Become thoroughly familiar with the manufacturer's operation and maintenance manual before using your hydrogen generator. Practice preventive maintenance.

It is recommended that the hydrogen generator be dedicated to use with the flame photometric detector and not shared with other analyzers. If two or more analyzers do share the same hydrogen generator, be sure that adequate pressure regulation and flow control is maintained to each analyzer.

All hydrogen generators, of course, produce oxygen concurrently. In some generators the oxygen is vented and not used. In others, the oxygen is dried and stored (under pressure) for laboratory use. The most trouble-free operation for FPD analyzers has been found with generators intended for hydrogen production only.

Certain precautions must be observed for successful, long-term, and safe use of hydrogen generators. Important points are:

1. Do not defeat the grounding three-wire power cord.
2. Fill the solution reservoir of the generator only with the manufacturer's specified solution.

> Exercise caution not to overfill the reservoir. If it is overfilled, water may be forced through the hydrogen line to the instrument. Follow the manufacturer's instructions.
>
> Some generators use only deionized distilled water. If water containing metallic impurities is used, the electrochemical cell will be damaged or contaminated. Deionization of the water may be required in the generator reservoir. Keep deionization bags or cartridges fresh.
>
> Other generators use caustic solutions of sodium hydroxide, or acidic solutions. Exercise care in handling these solutions.

3. Do not operate a hydrogen generator in a sealed or unvented room. Do not use near open flames or other sources of ignition.
4. Never allow the O_2 vent line to be obstructed.
5. Check the water or electrolytic solution level often. If the level gets low, the generator will cut off.
6. When first turning on the generator, allow it to develop a normal internal pressure before connecting to analyzers.
7. Change the desiccant cartridge often to maintain dry hydrogen gas. Be careful to reseal the desiccant cartridge carefully so it is leak-tight. Do not apply pressure to plastic parts with wrenches or other tools. To do so may cause cracking or stress lines and H_2 leakage could result.
8. Minimize the volume of hydrogen stored in lines and desiccant cartridges by minimizing the size of the line and the hydrogen pressure.

2.4 STARTUP OF AN FPD SO_2 ANALYZER

2.4.1 Power On; Warmup Times

With newer models of FPD SO_2 analyzers, only the main power switch (and perhaps an electronics switch) needs to be turned on. The air and fuel ignite automatically in a preprogrammed sequence. Since hydrogen gas does not flow to the analyzer until the power is turned on (the safety solenoid is closed in the power off mode), it may take several attempts before the flame lights. Most analyzers have a front panel lamp which indicates when the flame is lighted.

With older model analyzers, it is necessary to ignite the flame manually by depressing a switch which activates a "glow-plug" in the burner chamber. At times, it may be difficult to ignite the flame. One procedure to follow is this: engage the flame-out override feature; turn the hydrogen flow rate almost off by adjusting the hydrogen needle valve or rotameter on the instrument's front panel; depress the ignite switch; slowly increase the hydrogen flow while you continue to activate the ignite switch; when a "pop" is heard, or the ball of the hydrogen rotameter "bounces," release the ignite switch. Complete this operation in 5 seconds or less. Do not attempt to start ignition when any flow of hydrogen is present. Rapid ignition may damage the combustion chamber. If the flame is burning, the indicator lamp will be unlighted and the hydrogen rotameter will continue to indicate flow. Reset the rotameter ball to the desired or preset position. A significant change in hydrogen flow can alter the calibration.

Some older models of Meloy analyzers have the following feature which should be noted: a flame-out occurs (i.e., the H_2 solenoid closed) when the analyzer response voltage became negative. New models have a temperature sensor to detect an actual flame-out and cause the H_2 solenoid to close. Other early models lacked the hydrogen shut-off solenoid feature. If the flame went out, H_2 continued to flow. For such analyzers, be sure to vent the exhaust to the outside of the station.

A certain length of time will be required for the hydrogen to purge the air which may be present in the lines and give a mixture suitable for ignition at the burner tip. Other flame-out problems may be due to irregular or mismatched H_2/air sample flows, water condensation in the burner compartment, or a damaged or corroded burner tip, or mis-adjusted cams on instruments equipped with timers. Refer to the manufacturer's instruction manual for servicing and cleaning of burner compartments.

Warmup times may vary from instrument to instrument. It is a good idea to allow 24 hours before beginning calibration. A stable zero air or span gas trace on a strip chart recorder is a useful indicator of instrument stability.

Some analyzers have a flowmeter (rotameter) which indicates the flow of sample air through the instrument. Use this only for establishing or verifying a flow rate. Bypass this rotameter (by deactivating a solenoid valve) during the time of calibration or ambient air sampling.

2.4.2 "Peaking Up" Response Prior to Calibration

After the flame has burned for a few minutes, the air flow and the hydrogen flow should be adjusted to the manufacturer's recommended settings. The hydrogen flow is generally set by use of a rotameter. The sample air flow may also be set with a rotameter. This sample air rotameter should be bypassed in normal operation. A soap film flowmeter or mass flowmeter may also be used to determine and set the sample flow rate. Flow rates are generally around 150-200 cm^3/min.

Certain early models of Bendix analyzers have a burner tip whose height can be altered. The tip is threaded and can be moved up and down. This height is set at the factory. However, if the burner block is disassembled and cleaned, it may be necessary to test the analyzer with the burner tip at several different heights to optimize the signal. Consult your Bendix service representative for advice on the most efficient way to optimize the signal.

After the analyzer has warmed up, the operator proceeds to the calibration of the analyzer, described in Section 4.0 of this document. Calibration devices to generate known SO_2 concentrations are described in Section 3.0.

With new analyzers, the manufacturer supplies a "checkout sheet," which gives the results of the manufacturer's calibration and electrical constants for the particular analyzer. This sheet should be consulted during the initial calibration procedure. If your results do not agree fairly closely with the checkout sheet, the instrument may be damaged or improperly installed or your calibration and measurement system may be in error.

SECTION 3.0

GENERATION OF SO_2 CALIBRATION STANDARDS AND ZERO AIR

3.1 INTRODUCTION

The accuracy and validity of data derived from any air monitoring instrument is dependent upon the type and extent of quality control practices and procedures. Instrument calibration is the first element of data quality control and is the key to comparison and utilization of data produced by federal, state, local, and private air sampling networks.

Any monitoring instrument, such as the continuous FPD SO_2 analyzer, is subject to drift and variation in internal parameters and will need periodic calibration.

The recommended method of calibration is a direct, dynamic calibration utilizing the same pollutant species in the same air diluent as is being monitored. In the dynamic method, a known amount of pure or concentrated gaseous pollutant is mixed with diluting air as the mixture is used. A dynamic calibration of ambient air analyzers should generally be a multiple point calibration. That a multipoint calibration be performed is especially important in the case of the FPD, since its response is approximately proportional to the second power of SO_2 concentration and the more points, the better the calibration curve can be established. This calibration should be performed at the site of the analyzer (i.e., "in the field"). Reliable, portable equipment makes this possible. Many FPD analyzers now have linearized responses. Multipoint calibration is still important since in this way the operator will know that the linearization circuitry is properly adjusted. Another way to determine linearity is by simulating SO_2 response with a picoamp source. Consult the manufacturer's literature for details.

This section of the technical assistance document will discuss calibrator systems which may be used for generation of SO_2 gas standards for

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calibration of FPD as well as other types of SO_2 analyzers. The reproducibility, reliability, and accuracy of any system depends heavily on four aspects: reliable, known, certified sources of SO_2 (preferably NBS certified or NBS traceable); stable and accurately known temperatures of SO_2 permeating devices; known flow rates of dilution air; a proper source of zero or diluent air.

3.2 CLEAN AIR SOURCES FOR SO_2 CALIBRATION SYSTEMS

A source of clean, dry, sulfur-free air is necessary for various uses in all dynamic calibration systems. With FPD SO_2 analyzers, it is obvious that air, rather than nitrogen or some other inert gas, must be used since otherwise the detector flame would be extinguished. The nomenclature describing diluent air varies. Zero air is the name used when the clean air is sampled by the analyzer to allow the setting of the zero concentration signal output. Diluent air is the name given to air used to dilute a stream of air containing relatively high concentrations of SO_2. Sweep air or purge air is the term used when clean air sweeps or purges the effluent from a permeation tube or device.

This air must have certain characteristics in order to be employed in calibration of FPD SO_2 analyzers. Its water vapor content must be at levels where condensation does not occur; it must possess the ambient percentage (20.94) of oxygen found in air (since the flame of an FPD is sensitive to the oxygen/nitrogen ratio); it must retain ambient concentration levels of carbon dioxide, CO_2, (since the FPD has some degree of sensitivity to CO_2); and of course it must be free of all sulfur-containing compounds.

Since the same source of air is often used to prepare zero and calibration gas for other pollutant monitors, removal of other pollutants is another desirable feature.

3.2.1 Zero Air Generators

Figure 3.1 shows the basic components and general specifications of a zero air generator which will produce air suitable for use in calibration of FPD SO_2 analyzers.[14] Greater details on this system are given in the reference. Such a system is suitable for 99 percent removal of nitric oxide, NO, NO_2, SO_2, H_2S, and other pollutant gases. It allows CO_2 in ambient air to pass through unaffected.

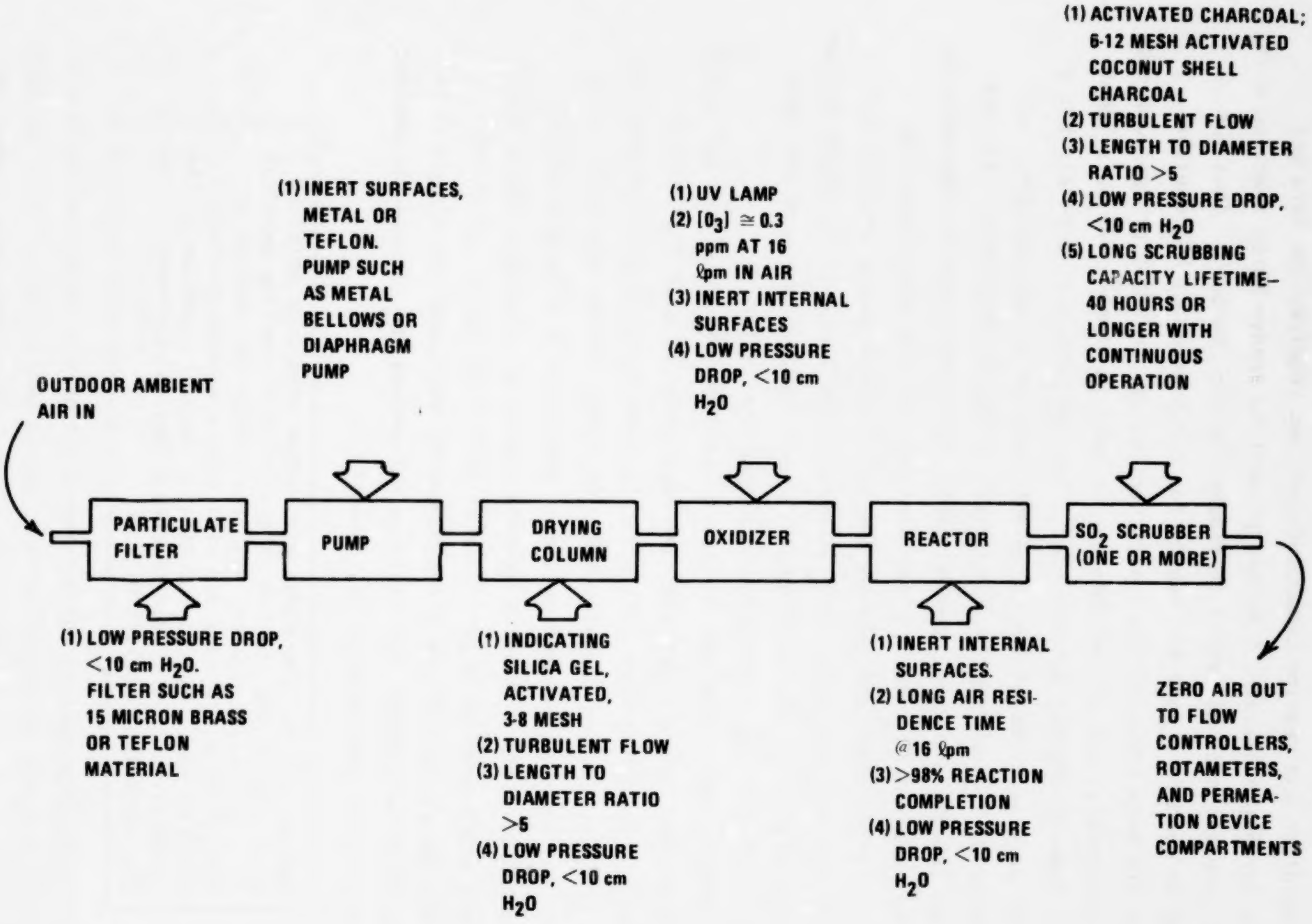

OUTDOOR AMBIENT AIR IN
PARTICULATE FILTER
PUMP
DRYING COLUMN
OXIDIZER
REACTOR
SO_2 SCRUBBER (ONE OR MORE)
ZERO AIR OUT TO FLOW CONTROLLERS, ROTAMETERS, AND PERMEATION DEVICE COMPARTMENTS
(1) LOW PRESSURE DROP, <10 cm H_2O. FILTER SUCH AS 15 MICRON BRASS OR TEFLON MATERIAL
(1) INERT SURFACES, METAL OR TEFLON. PUMP SUCH AS METAL BELLOWS OR DIAPHRAGM PUMP
(1) INDICATING SILICA GEL, ACTIVATED, 3-8 MESH
(2) TURBULENT FLOW
(3) LENGTH TO DIAMETER RATIO >5
(4) LOW PRESSURE DROP, <10 cm H_2O
(1) UV LAMP
(2) $[O_3] \cong 0.3$ ppm AT 16 ℓpm IN AIR
(3) INERT INTERNAL SURFACES
(4) LOW PRESSURE DROP, <10 cm H_2O
(1) INERT INTERNAL SURFACES.
(2) LONG AIR RESIDENCE TIME @ 16 ℓpm
(3) >98% REACTION COMPLETION
(4) LOW PRESSURE DROP, <10 cm H_2O
(1) ACTIVATED CHARCOAL; 6-12 MESH ACTIVATED COCONUT SHELL CHARCOAL
(2) TURBULENT FLOW
(3) LENGTH TO DIAMETER RATIO >5
(4) LOW PRESSURE DROP, <10 cm H_2O
(5) LONG SCRUBBING CAPACITY LIFETIME—40 HOURS OR LONGER WITH CONTINUOUS OPERATION

Figure 3.1. Zero air generator suitable for FPD SO_2 zero and calibration.

The oxidizer and reactor components are not required for zero gas production for SO_2 analyzers; they are present to remove NO by reaction with ozone and conversion to NO_2 which is removed by the charcoal. Thus the system may be used as a zero air source for calibration of NO_x monitors.

There are many types of clean air supplies in use which process ambient air. Unfortunately, not all of them can be used to supply zero or diluent air to any type of ambient air analyzer. The definition of zero air has a meaning not only in terms of the pollutant response of the analyzer, but also in terms of the analyzer's interferent molecular responses. For the case of the FPD SO_2 analyzer, zero air must not contain sulfur compounds but must contain ambient CO_2 levels. For instance, it has been found that heatless air dryer clean air systems are not suitable as calibration air sources for the FPD analyzer. This is because the heatless air dryer system selectively retains CO_2 on the molecular sieve dryer column, and the back-flush cycle prevents CO_2 from passing through the system.

If the air supply requires drying, a Drierite (TM) or silica gel scrubber is suggested. These materials have been shown to pass CO_2 without diminishment. The Perma-Pure (TM) dryer is also an acceptable alternative.

Any air supply which contains Ascarite, soda lime or other air scrubbers known to remove CO_2 cannot be used. Regenerative molecular sieve dryers cannot be used. Activated alumina dryers or scrubbers should also not be used since alumina is partially selective in absorption of CO_2.

If the CO_2 content of the air produced by the clean air system(s) in your laboratory is unknown, it should be determined and compared to ambient air concentrations determined simultaneously.

> Ambient air for the clean air system should be obtained from outside the station (the station's sampling manifold is a convenient source) not from within the station or laboratory since room air will have elevated concentrations of CO_2. The CO_2 content of the air produced by the clean air supply should be determined and compared to the CO_2 content of ambient air.

A gravimetric procedure for determination of CO_2 concentration in air (by absorption of CO_2 on Ascarite) is given in Section 5.0 of this document. Determinations done simultaneously on air from the calibration system and from ambient air should match fairly well. If the CO_2 content from the calibration system is much lower than that of ambient air, the system should be improved.

3.2.2 Compressed Air Cylinders

Compressed air cylinders or other compressed air supplies are also used to supply air for calibration purposes. It is important that this air have the following properties for use with FPD analyzers:

a. The same O_2 and N_2 percentage composition as ambient air (20.94% O_2, 78.08% N_2).

b. A CO_2 content similar to that of ambient air, somewhere between 300 and 350 ppm. If the average CO_2 at a particular monitoring site is significantly greater than 350 ppm, then the cylinder should contain the higher level. One way to specify this when ordering would be to order a specialty gas mixture of CO_2 (350 ppm) in zero air.

If this air contains sulfur compounds and/or particulate matter, it must be cleaned by passage through an activated charcoal scrubber system and/or a particulate filter.

For calibration systems based on dilution of high level cylinder concentrations of SO_2 in air or nitrogen, the presence of ambient concentrations of CO_2 within the SO_2 standard cylinder is not necessary if the sample: air dilution ratio is small (such as 1:500) and the diluent air is zero air containing ambient concentrations of CO_2.

On the other hand, if low-level SO_2 in air cylinders are used for calibration or audit checks, the cylinder should contain ambient levels of CO_2 since the contents of the cylinder will be routed directly to the calibration manifold with little or no dilution.

3.3 PERMEATION TUBES AND DEVICES CONTAINING LIQUEFIED SO_2: CHARACTERISTICS AND USE

3.3.1 Introduction

A liquifiable gas, when enclosed in an inert plastic tube (i.e., Teflon), escapes by permeating the wall at a constant, reproducible, temperature-dependent rate. The rate of escape of gaseous SO_2 from a permeation tube is determined gravimetrically. The weight loss of the tube is equated to the weight of the escaping material. Further background information concerning the theory, construction, and behavior of permeation tubes or devices can be found in the literature.[15,16,17,18,19]

Today, most SO_2 permeation tubes are purchased directly from suppliers with the rate of permeation (stated in micrograms/minute or nanograms/minute) pre-established. For ambient air calibration work, a reliable source of permeation tubes in the United States is the National Bureau of Standards (NBS). The NBS permeation tube is in fact a Standard Reference Material, SRM. If another supplier is employed, be sure to request a calibration certificate which states that the tube's permeation rate is traceable to NBS Standard Reference Material.

Some calibrators may use only special permeation devices. These are not tubes but are wafers or cylinders. Such devices should also be purchased with certificates of traceability to NBS standards or be compared in the laboratory to an NBS Standard Reference Material.

3.3.2 Description of NBS Permeation Tubes

The National Bureau of Standards supplies three different size SO_2 permeation tubes. A diagram of a tube is shown in Figure 3.2. Each tube is calibrated individually and is certified as a Standard Reference Material (SRM). They are:

SRM No.	Size	Nominal Permeation Rate at 25° C
1627	2 cm	0.56 micrograms/minute
1626	5 cm	1.4 micrograms/minute
1625	10 cm	2.8 micrograms/minute

Figure 3.3 is a copy of the NBS Certificate for SRM No. 1626. It lists the method of calibration of the tube and gives use and storage information.

Table 3.1 is a copy of a table which shows the relationship between temperature and permeation rate for an actual NBS permeation tube. The table also gives an equation of the form $\log R = mt + b$ which can be used to compute permeation rates at other temperatures within the range of certification. Caution! This equation applies only to tube number 33-64.

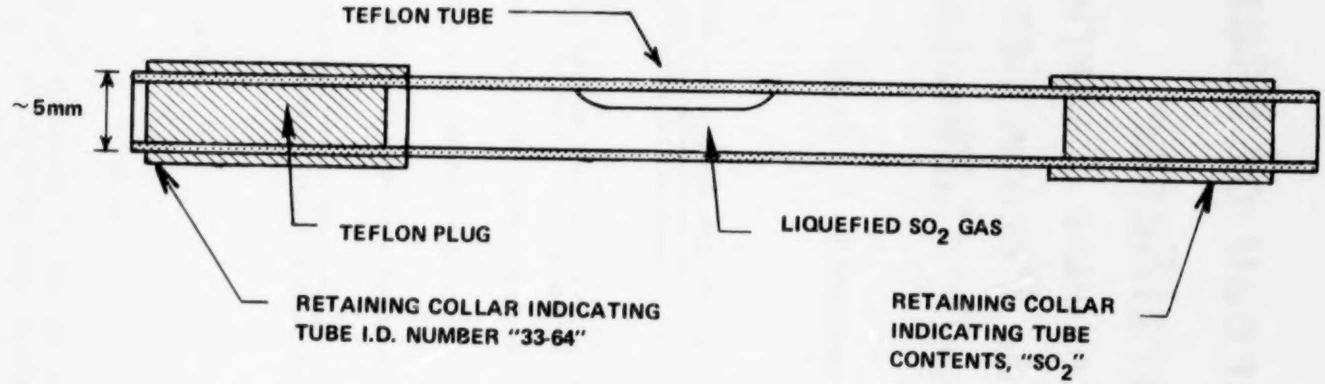
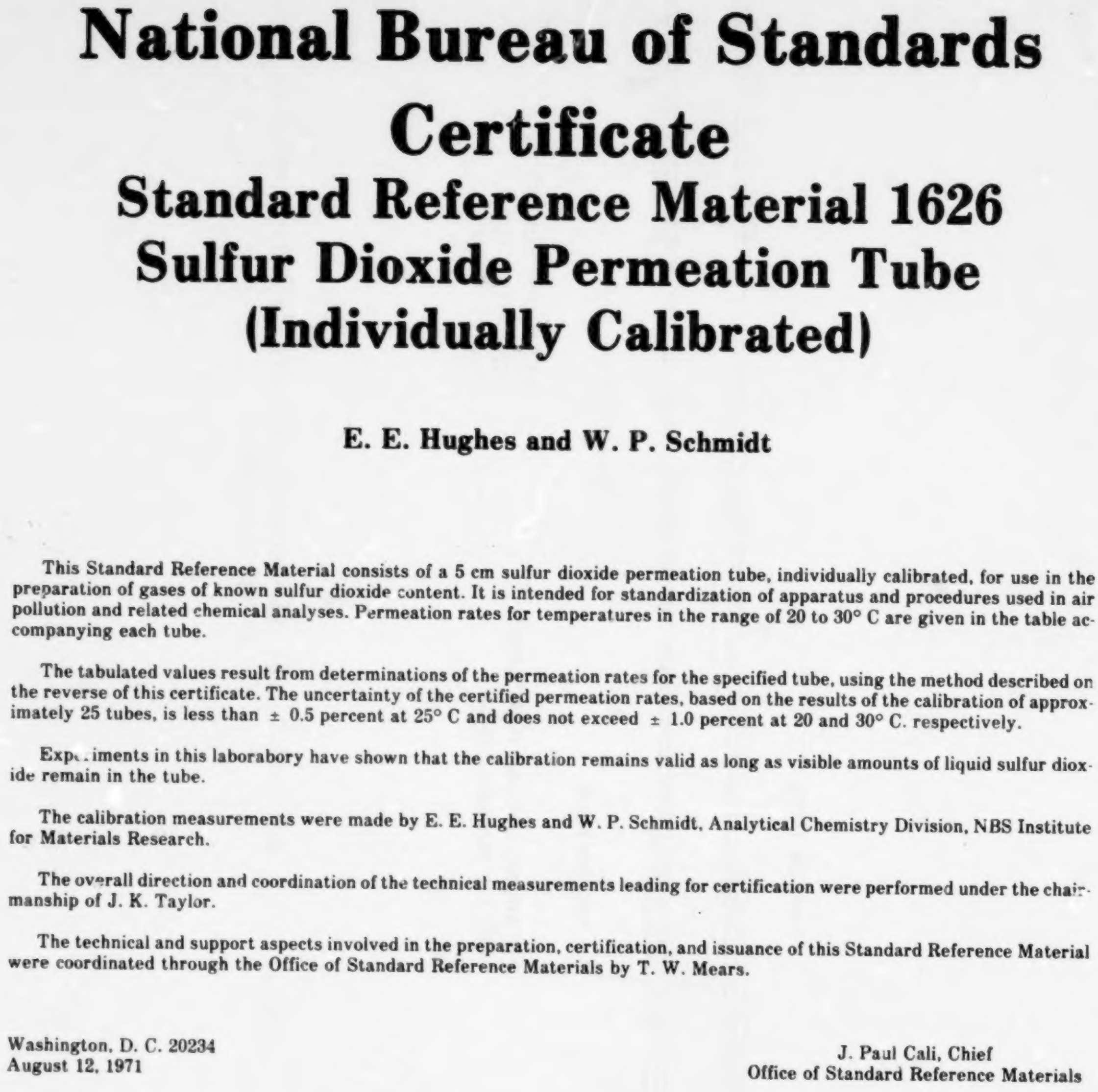

TEFLON TUBE
~5mm
TEFLON PLUG
LIQUEFIED SO2 GAS
RETAINING COLLAR INDICATING TUBE I.D. NUMBER "33-64"
RETAINING COLLAR INDICATING TUBE CONTENTS, "SO2"

Figure 3.2. National Bureau of Standards standard reference material SO_2 permeation tube.



National Bureau of Standards
Certificate
Standard Reference Material 1626
Sulfur Dioxide Permeation Tube
(Individually Calibrated)

E. E. Hughes and W. P. Schmidt

This Standard Reference Material consists of a 5 cm sulfur dioxide permeation tube, individually calibrated, for use in the preparation of gases of known sulfur dioxide content. It is intended for standardization of apparatus and procedures used in air pollution and related chemical analyses. Permeation rates for temperatures in the range of 20 to 30° C are given in the table accompanying each tube.

The tabulated values result from determinations of the permeation rates for the specified tube, using the method described on the reverse of this certificate. The uncertainty of the certified permeation rates, based on the results of the calibration of approximately 25 tubes, is less than ± 0.5 percent at 25° C and does not exceed ± 1.0 percent at 20 and 30° C. respectively.

Experiments in this laborabory have shown that the calibration remains valid as long as visible amounts of liquid sulfur dioxide remain in the tube.

The calibration measurements were made by E. E. Hughes and W. P. Schmidt, Analytical Chemistry Division, NBS Institute for Materials Research.

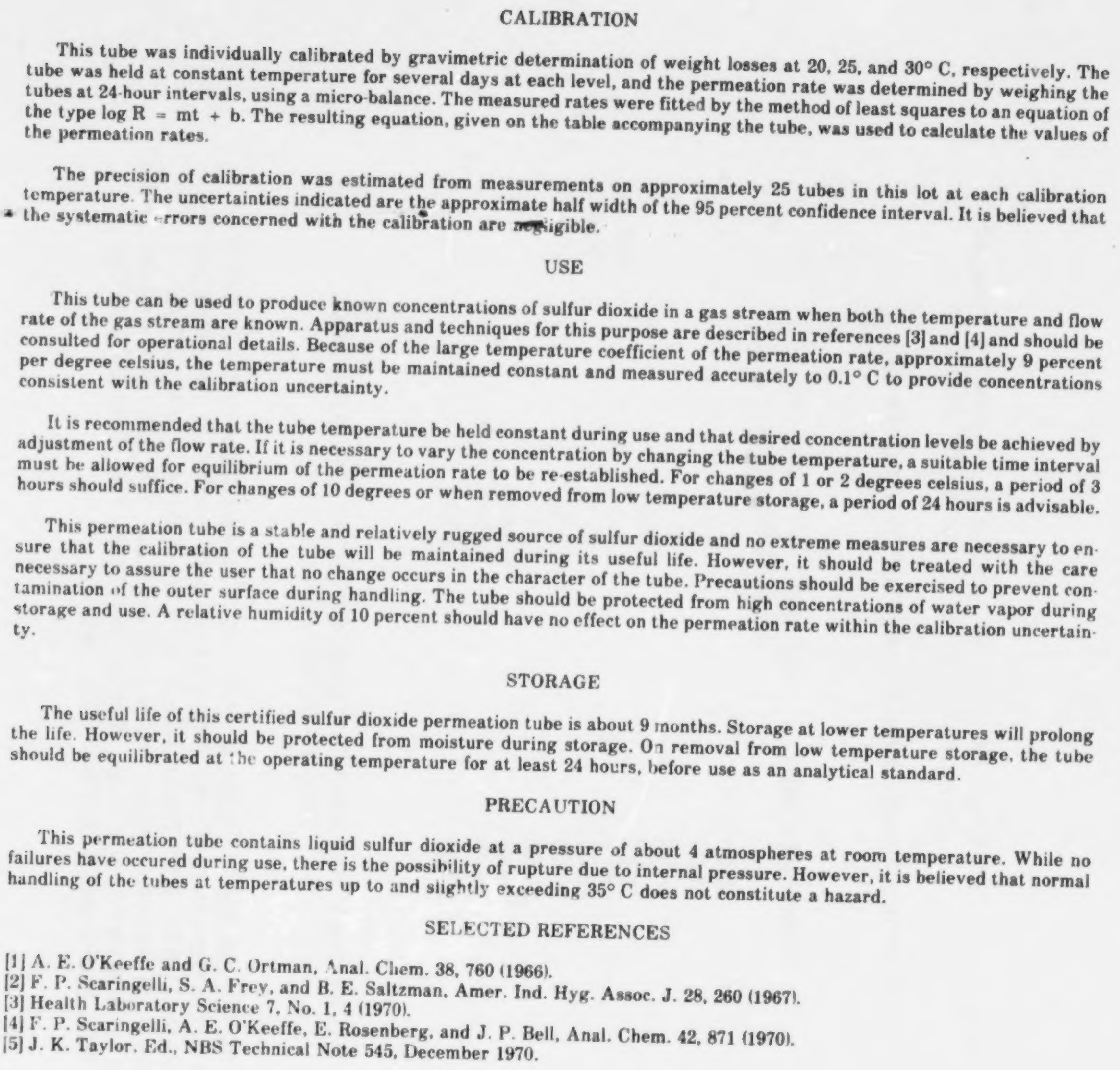
The overall direction and coordination of the technical measurements leading for certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
August 12, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

Figure 3.3. National Bureau of Standards sulfur dioxide permeation tube certificate



CALIBRATION

This tube was individually calibrated by gravimetric determination of weight losses at 20, 25, and 30° C, respectively. The tube was held at constant temperature for several days at each level, and the permeation rate was determined by weighing the tubes at 24-hour intervals, using a micro-balance. The measured rates were fitted by the method of least squares to an equation of the type $\log R = mt + b$. The resulting equation, given on the table accompanying the tube, was used to calculate the values of the permeation rates.

The precision of calibration was estimated from measurements on approximately 25 tubes in this lot at each calibration temperature. The uncertainties indicated are the approximate half width of the 95 percent confidence interval. It is believed that the systematic errors concerned with the calibration are negligible.

USE

This tube can be used to produce known concentrations of sulfur dioxide in a gas stream when both the temperature and flow rate of the gas stream are known. Apparatus and techniques for this purpose are described in references [3] and [4] and should be consulted for operational details. Because of the large temperature coefficient of the permeation rate, approximately 9 percent per degree celsius, the temperature must be maintained constant and measured accurately to 0.1° C to provide concentrations consistent with the calibration uncertainty.

It is recommended that the tube temperature be held constant during use and that desired concentration levels be achieved by adjustment of the flow rate. If it is necessary to vary the concentration by changing the tube temperature, a suitable time interval must be allowed for equilibrium of the permeation rate to be re-established. For changes of 1 or 2 degrees celsius, a period of 3 hours should suffice. For changes of 10 degrees or when removed from low temperature storage, a period of 24 hours is advisable.

This permeation tube is a stable and relatively rugged source of sulfur dioxide and no extreme measures are necessary to ensure that the calibration of the tube will be maintained during its useful life. However, it should be treated with the care necessary to assure the user that no change occurs in the character of the tube. Precautions should be exercised to prevent contamination of the outer surface during handling. The tube should be protected from high concentrations of water vapor during storage and use. A relative humidity of 10 percent should have no effect on the permeation rate within the calibration uncertainty.

STORAGE

The useful life of this certified sulfur dioxide permeation tube is about 9 months. Storage at lower temperatures will prolong the life. However, it should be protected from moisture during storage. On removal from low temperature storage, the tube should be equilibrated at the operating temperature for at least 24 hours, before use as an analytical standard.

PRECAUTION

This permeation tube contains liquid sulfur dioxide at a pressure of about 4 atmospheres at room temperature. While no failures have occured during use, there is the possibility of rupture due to internal pressure. However, it is believed that normal handling of the tubes at temperatures up to and slightly exceeding 35° C does not constitute a hazard.

SELECTED REFERENCES

[1] A. E. O'Keeffe and G. C. Ortman, Anal. Chem. 38, 760 (1966).
[2] F. P. Scaringelli, S. A. Frey, and B. E. Saltzman, Amer. Ind. Hyg. Assoc. J. 28, 260 (1967).
[3] Health Laboratory Science 7, No. 1, 4 (1970).
[4] F. P. Scaringelli, A. E. O'Keeffe, E. Rosenberg, and J. P. Bell, Anal. Chem. 42, 871 (1970).
[5] J. K. Taylor, Ed., NBS Technical Note 545, December 1970.

Figure 3.3. National Bureau of Standards sulfur dioxide permeation tube certificate (con.)

Table 3.1. Certified permeation rates for National Bureau of Standards permeation tube No. 33-64.

CERTIFIED PERMEATION RATES FOR TUBE NO. 33- 64

CAUTION! EXAMPLE ONLY!

TEMPERATURE C	PERMEATION RATE, SO2 MICROGRAM/MIN
20.00	.832
21.00	.899
22.00	.972
23.00	1.050
24.00	1.135
25.00	1.227
26.00	1.326
27.00	1.433
28.00	1.549
29.00	1.674
30.00	1.810

CAUTION! EXAMPLE ONLY!

THE PERMEATION RATE IS REPRESENTED BY THE EQUATION

$$\text{LOG } R = M(273.15+T)-B$$

WHERE $M = .033759$, $B = 9.97634$ AND T IS TEMPERATURE IN DEGREES C THIS EQUATION MAY BE USED TO CALCULATE RATES AT INTERMEDIATE TEMPERATURES, NOT TABULATED, AND TO ESTIMATE VALUES AT TEMPERATURES NOT MORE THAN 2 DEGREES C. BEYOND THE RANGE OF THE TABLE. HOWEVER, THE TUBE IS NOT CERTIFIED FOR TEMPERATURES OUTSIDE THE RANGE GIVEN IN THE TABLE.

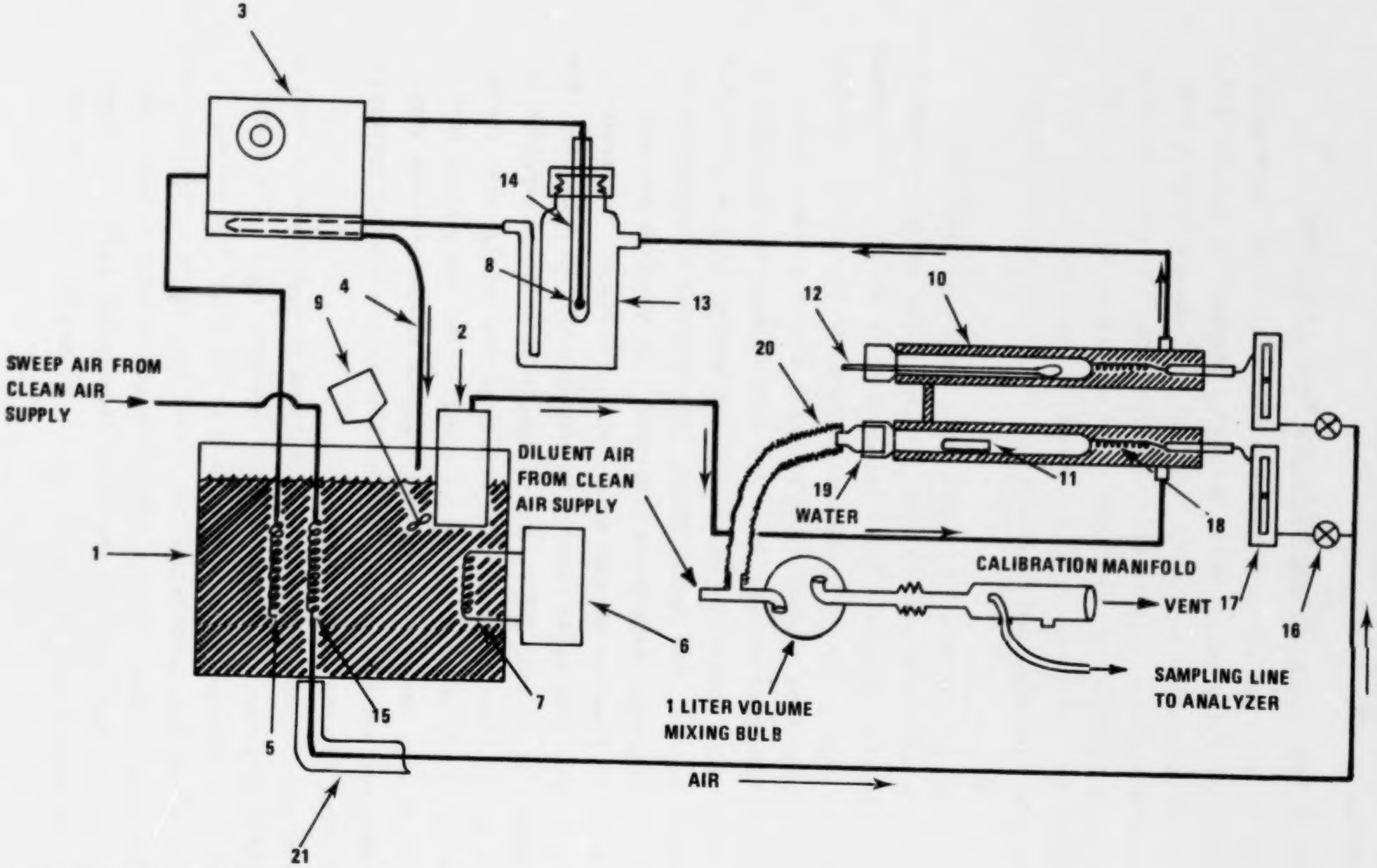
3.4 CALIBRATION SYSTEMS BASED ON PERMEATION DEVICES: DESCRIPTION AND EXPLANATION OF USE

3.4.1 Custom-built Laboratory Systems Employing Permeation Tubes

Many SO_2 calibration gas sources have been custom-built for laboratory use. Such systems generally employ water baths for temperature control and glass condensers as permeation tube holders. Such systems are inconvenient for use in the field because of their bulk and fragility. A system suitable for generation of SO_2 atmospheres (and with minor modification, H_2S and NO_2) is shown in Figure 3.4. A schematic of a laboratory clean air supply is shown in Figure 3.5. The numbered components of the system are discussed below.

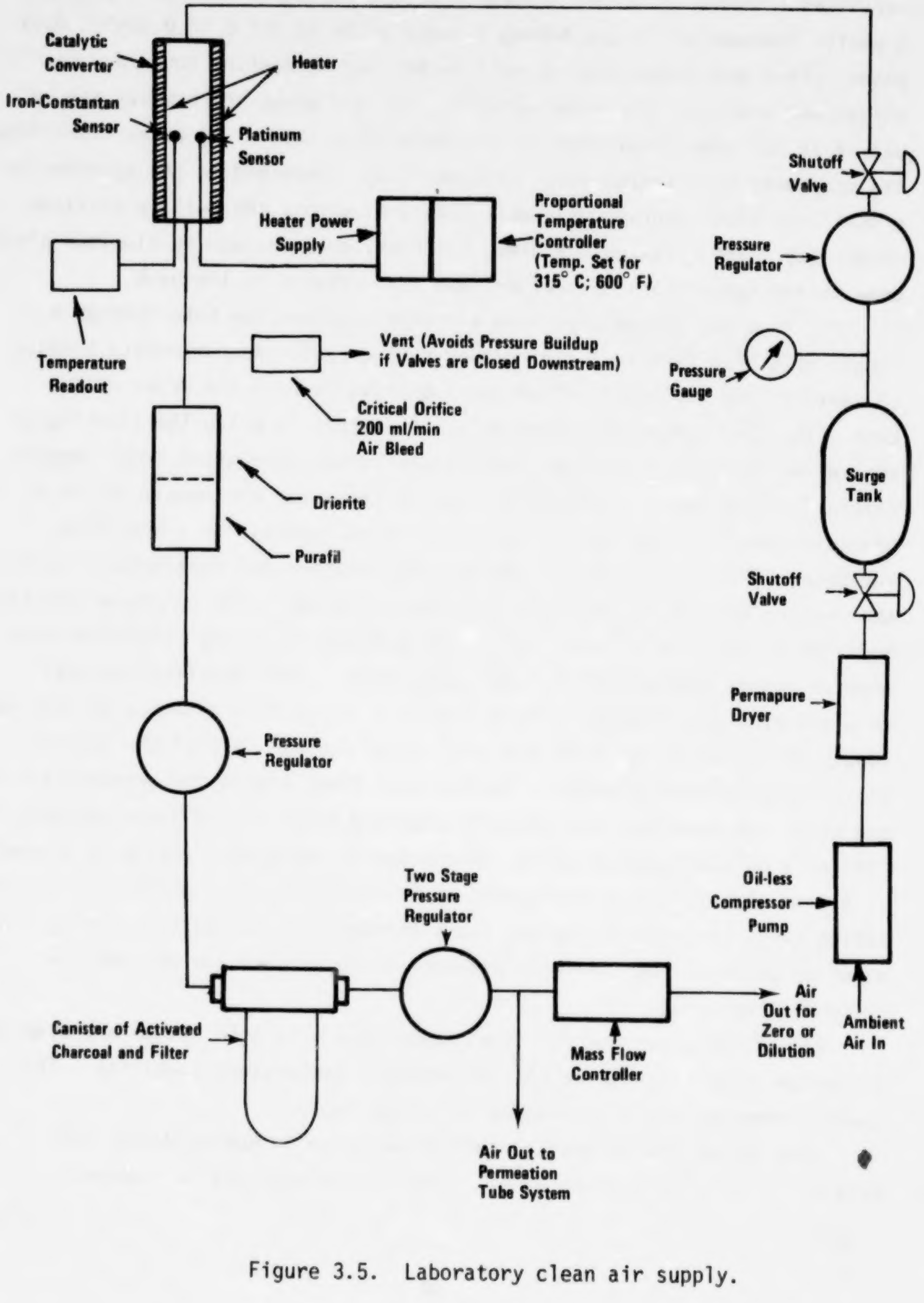
The system shown in Figure 3.5 is built around a "Forma Temp Jr." constant temperature water circulating bath (1), which has an approximate 8 liter (2 gallon) capacity, controls water temperature to ±0.1°C, by alternate heating and cooling, has a variable temperature range of 15 to 35°C, and has a positive displacement type recirculating pump (2) with a 1 l/min liquid flow rate. The heating/cooling portion of the bath is modified by adding a proportional temperature controller No. 71 (3) and control dial manufactured by RFL Industries, Boonton, New Jersey 07005. The electronic components of the controller are somewhat temperature sensitive. By mounting the controller on a block of aluminum through which water circulates, temperature stability is achieved. The water returns to the bath through tube (4). For temperature control at or near 25° C, approximately 30 volts is supplied to the heater (5) at all times to "buck" the effect of the refrigerated cooler (6) and cooler coils (7) which are on at all times. The temperature controller applies varying smaller voltages in response to the platinum sensor (8). If the need for additional water circulation in the tank is indicated, a motorized stirrer (9) should be added.

Water from the constant temperature bath flows through rubber tubing to one or more water-jacketed, large-bore glass condensers (10). The glass condensers are at a constant temperature and keep the airstream moving through them at a constant temperature too. Keep the length of tubing used to supply water to a minimum. The straight condenser (Liebig or West type) houses the permeation tube (11) and the glass thermometer (12). The thermometer gives the temperature of the air and the permeation tube. An NBS


3
14
8
4
9
2
13
10
12
20
SWEEP AIR FROM
CLEAN AIR
SUPPLY
DILUENT AIR
FROM CLEAN
AIR SUPPLY
1
11
19
WATER
18
CALIBRATION MANIFOLD
VENT 17
16
6
7
15
5
1 LITER VOLUME
MIXING BULB
SAMPLING LINE
TO ANALYZER
AIR
21

Components are described by number in the text.

Figure 3.4. Example of custom-made laboratory permeation tube assembly for calibration of SO_2 analyzers.



Catalytic Converter
Heater
Iron-Constantan Sensor
Platinum Sensor
Heater Power Supply
Proportional Temperature Controller (Temp. Set for 315° C; 600° F)
Temperature Readout
Vent (Avoids Pressure Buildup if Valves are Closed Downstream)
Critical Orifice 200 ml/min Air Bleed
Drierite
Purafil
Pressure Regulator
Canister of Activated Charcoal and Filter
Two Stage Pressure Regulator
Mass Flow Controller
Air Out to Permeation Tube System
Air Out for Zero or Dilution
Ambient Air In
Oil-less Compressor Pump
Permapure Dryer
Shutoff Valve
Surge Tank
Pressure Gauge
Pressure Regulator
Shutoff Valve

Figure 3.5. Laboratory clean air supply.

certified thermometer or one traceable to NBS standards should be employed. A useful thermometer is one having a range of 24 to 25° C in 0.005° C divisions, since many commercial as well as NBS SO_2 permeation tubes are certified and used over the range 20-30°C. The all glass thermometer may be placed in the same compartment as the permeation tube. The water flows from the condenser to a sealed glass cylinder (13). Attached to the cylinder is a stainless steel thermocouple well (14) and, within the well, a platinum sensor (8). Water leaves the glass cylinder, goes through an aluminum block beneath the temperature controller, and then returns to the bath.

Air from the laboratory clean air supply enters the bath through a length of 6.3 mm (1/4 in.) o.d. copper tubing (15). Approximately 1 meter (3 feet) of the tubing is coiled and submerged beneath the water of the bath. The coil serves as a heat exchange element to bring the flushing or carrier air to nearly the same temperature as the permeation tube. Appropriate fittings connect the copper tube to the clean air supply and to a precision needle valve (16). The needle valve connects to a precision rotameter (17) having a flow range between zero and 500 cc/minute. The air then enters one end of the water jacketed condenser. The condenser has been modified so that the air will be at the temperature of the permeation tube when it enters the permeation tube compartment. This modification (18) consists of a short length of 0.25 inch o.d. glass tube attached to a 3 inch length of coiled 3.2 mm (1/8 in.) o.d. glass tubing. All of the coiled glass is surrounded by water. The air then flows across the permeation tube and exits the condenser via either a standard taper ground glass connector (19) or a ball and socket joint. Connected to the glass fitting is a length of 6.3 mm (1/4 in.) o.d. corrugated or conventional, straight-walled Teflon tubing (20). Air containing SO_2 flows through this tubing to a mixing flask at which point it combines with diluent air to produce the desired low concentration of SO_2.

All of the water and air lines associated with this system are wrapped in sponge rubber insulation (21) to maintain temperature stability. The glass condensers are also wrapped in sponge rubber.

Flow across the permeation tube is adjusted to approximately 200 cc/min. Flow is maintained at all times unless the tube is removed.

Attention should be given to the air supply used with the laboratory system. Ambient levels of O_2 (20.94%) and CO_2 (~350 ppm) should be present in both the flushing or carrier air and the diluent or zero air. The air supply system shown in Figure 3.5 is designed to run continuously. The source of air should be "outside" ambient air to ensure that O_2 and CO_2 levels in the calibration gas are equivalent to those levels in the actual "outside" sample air.

3.4.2 Commercial Systems Employing Permeation Tubes or Devices

Many brands and types of SO_2-producing "calibrators" are available commercially. All of them depend on control of the temperature of the permeation tube or device and control of the flow of air across the tube and the flow of diluent air in order to produce a known final concentration of SO_2 in air within the calibration manifold. Figure 3.6 is a schematic of the components of a typical calibrator intended for SO_2 production only. Figure 3.7 is a schematic of a more elaborate calibrator system intended for multi-pollutant calibration work. Refer to Section 3.2 for further discussion of zero air supplies for calibrators intended for use with FPD SO_2 analyzers.

The temperature of the permeation tube or device is set and controlled in one of several ways. Some systems employ a small recirculating water bath. Many systems have a thermostatted "air bath" in which the permeation device holder is mounted. Others employ heated metal blocks. Whatever the system, it is important that the temperature be known and controllable to ±0.1° C since the permeation rate of a tube or device is extremely sensitive to temperature (see Table 3.2).

The flow of air across the permeation device as well as the flow of diluent air is regulated in one or more of several ways. The simplest systems have a rotameter and an adjustable needle valve to set and control the air flows. Such rotameters must be calibrated and checked frequently. A rotameter should be calibrated "in-line," that is, while it is an installed part of the system, and not separate from the calibration system. Do not rely solely on a "calibration curve" for the rotameter. Use a soap film flowmeter or wet test meter to check flows. More sophisticated systems employ critical orifices or long lengths of stainless steel capillary tubing

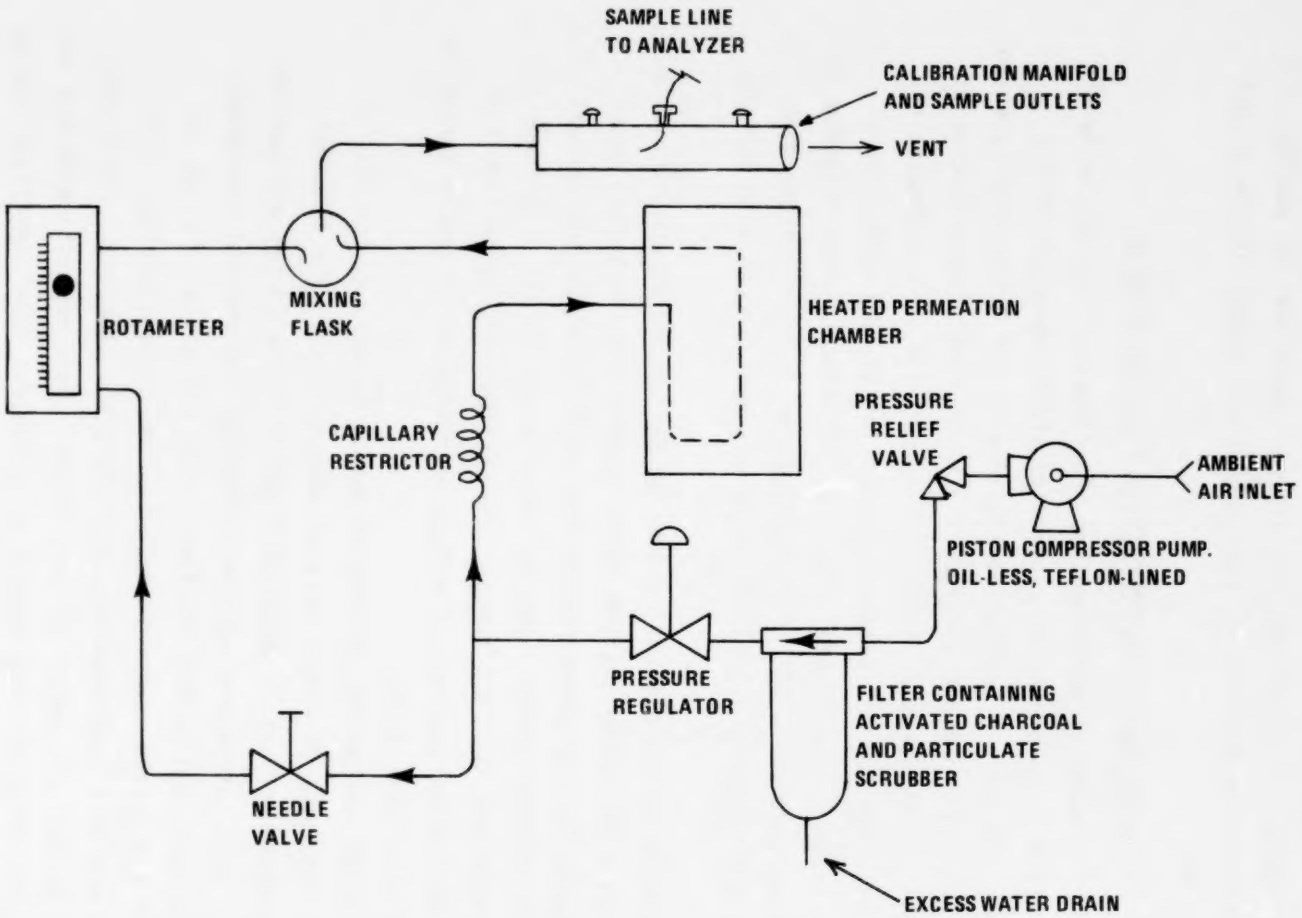

SAMPLE LINE
TO ANALYZER
CALIBRATION MANIFOLD
AND SAMPLE OUTLETS
VENT
ROTAMETER
MIXING
FLASK
HEATED PERMEATION
CHAMBER
CAPILLARY
RESTRICTOR
PRESSURE
RELIEF
VALVE
AMBIENT
AIR INLET
PISTON COMPRESSOR PUMP.
OIL-LESS, TEFLON-LINED
PRESSURE
REGULATOR
FILTER CONTAINING
ACTIVATED CHARCOAL
AND PARTICULATE
SCRUBBER
NEEDLE
VALVE
EXCESS WATER DRAIN

Figure 3.6. Schematic diagram of a portable SO_2 calibrator with internal air supply.

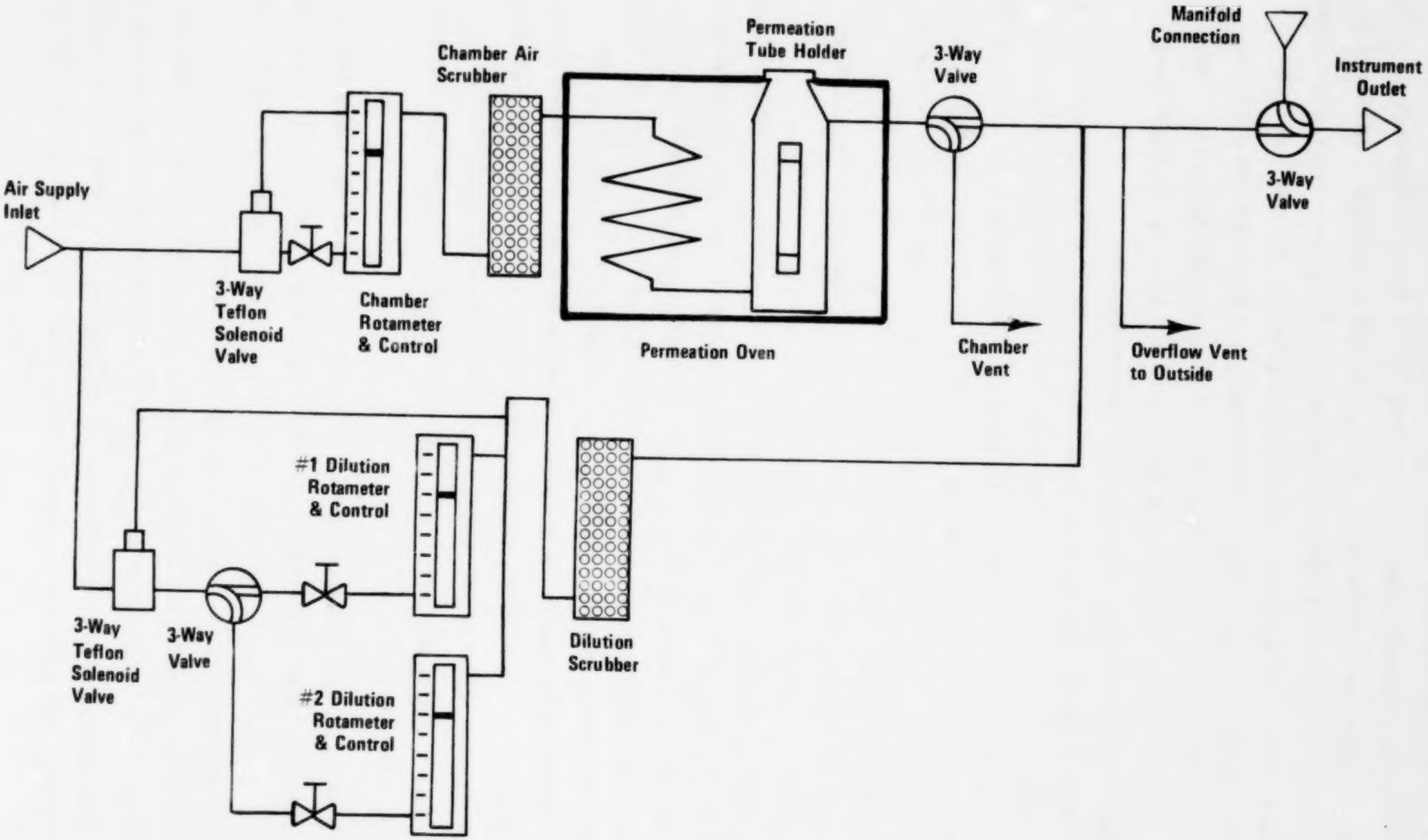

Air Supply Inlet
3-Way Teflon Solenoid Valve
Chamber Rotameter & Control
Chamber Air Scrubber
Permeation Tube Holder
Permeation Oven
3-Way Valve
Chamber Vent
Overflow Vent to Outside
Manifold Connection
Instrument Outlet
3-Way Valve
#1 Dilution Rotameter & Control
#2 Dilution Rotameter & Control
Dilution Scrubber
3-Way Teflon Solenoid Valve
3-Way Valve

Figure 3.7. Schematic diagram of multipollutant calibrator. (Adapted from Metronics Association, Inc. "Dynacalibrator").

to control air flow. Oftentimes regulators and pressure dials are present so that flow can be re-established by "dialing in" a certain pressure on the capillary tube or a network of tubes. Even with these systems, calibration and frequent checks of air flow versus pressure setting are necessary. Some calibrators have mass flow controllers which can be set to deliver predetermined mass flows of air. Since mass flowmeters are not infallible, they too must be calibrated or verified and rechecked periodically. Mass flowmeters often exhibit a temperature sensitivity; thus it is important to operate them at controlled, reproducible temperatures.

All flow measurements taken must be corrected to standard conditions of pressure and temperature: 760 mm Hg and 25°C for air pollution work. If a soap film flowmeter or wet test meter is used, do not neglect to correct for the effect of water vapor (explained in Section 5, Procedural Aids) since the calibration air is usually quite dry and picks up water vapor while a flow is being established.

The following features are recommended for consideration in a commercial SO_2 "calibrator" which employs a permeation tube or device.

1. The presence of a means for temperature control and verification. Some "calibrators" have a fixed, unchangeable temperature. If temperature can be varied, a thumbwheel or digital system for accurately setting and resetting temperatures should be present. A device (such as flashing light or meter/needles) should be present to indicate when the desired temperature has been attained or when the desired temperature is not present. Attainment of the temperature of course does not mean that the permeation tube or device has also attained equilibrium. Generally, an additional 24 to 48 hours should be allowed for permeation tube equilibrium.

   Ideally, an accurate thermometer or thermistor should be embedded in the permeation tube compartment so that any temperature variations can be read directly. This thermometer or thermistor should be installed in such a way that upon removal and replacement, it is seated in exactly the same geometrical configuration. In other words, it should be impossible for the operator to re-install the thermometer or thermistor in any way except the correct way. If a temperature sensing device is not included, the calibrator should have some way to allow the operator to reproducibly place a temperature measuring device in the vicinity of the permeation device.

2. The permeation tube or device should be easily inserted and removed. Connections to the permeation tube holder should be leak-tight and easily retightened and repositioned. All lines downstream of the permeation tube oven should be of Teflon or glass construction.
3. Air flow controllers and indicators should be of the highest quality and be capable of being set reproducibly. For instance, pressure gauges should have accurately divided fine graduations and rotameters should be of sufficient length (12 inches preferred) to give good resolution in reading.
4. For field use in calibration of ambient air monitors, the "portability option" is highly recommended. This option permits a car battery to supply power to the "calibrator" to keep the oven warm and equilibrated and to run a small pump to allow continuous passage of air over the permeation tube or device. If such an option is not used, it is necessary to either remove the permeation tube or purge the system for some time before use since the high concentrations of SO_2 which have built up will be released slowly from Teflon components. It is also, of course, necessary to re-equilibrate the permeation tube or device at the desired temperature. While the permeation tube or device is warming up (equilibrating), a flow of air should pass over the tube or device.
5. For field use, an internal source of air is desirable. Usually a small diaphragm or bellows pump is employed. This does away with the necessity of providing an external air source and gives a reproducible source of air from site to site. Certain precautions must be taken when using such an air supply. Necessary scrubbers and filters must be changed periodically. The O_2 and CO_2 content of the air produced must be characterized and be maintained near the values for ambient air. Provisions must be included for drying the air and venting any excess moisture buildup caused by compression of air by the pump. The flow of air from such internal sources must be stable. The best systems employ differential pressure regulators. Such regulators can give very stable

flow and can be used with internal air supplies or external air supplies such as compressed air cylinders.

6. Since the "calibrator" is often used as a source of zero air, it is recommended that some sort of zero air by-pass loop be present. In this way the permeation tube compartment is either by-passed or its effluent is flushed.

7. The possibility for use of an NBS Standard Reference Material permeation tube in the calibrator should be considered. Not all calibrators offer this feature since other permeation tubes or devices are either of smaller dimensions than NBS tubes or operate at higher temperatures than those specified for NBS tubes. If your calibrator does not have this feature, it is recommended that a line of traceability of your system to another system which does use an NBS tube be established. Also, permeation tubes or devices may be purchased which are traceable to NBS Standard Reference Materials.

8. The possible range of SO_2 concentrations and the range of air flows desired is also a consideration. Various SO_2 analyzers require different sample flow rates.

3.4.3 Explanation of Use of Permeation Device Calibration Systems

The instructions listed below can be applied to most permeation device type calibration systems for SO_2. Use the operation manual for your particular calibrator in conjunction with these instructions and explanations.

1. Unpack and inspect the calibrator. Always perform an inspection if the calibrator has been shipped to a new location. Inspect the apparatus (especially the flowmeters and needle valves) for shipping damage. Look inside the case for evidence of broken or loose mixing tees or bulbs, loose electronic boards, etc.

2. Make electrical connections. First, be sure that all power switches are in the "off" position or "stand by" position. Connect the power switch to a 115V AC socket using a grounded 3-prong plug. Turn the main power switch to "on" and check the following: internal air supply pump is on; the fan for air circulation is on and the fan blades spin freely; the heater for the permeation tube bath or oven is on. This should be indicated by a temperature light or dial. Turn off the main power.

3. Connect the air supply to the calibrator. If the calibrator has its own internal zero air supply, connect the inlet of the air supply pump to the station sampling manifold so that ambient air is treated by the cleanup system. If a separate air supply system is used, connect its inlet to an outdoor ambient air source. Do not use room air since it will have a high CO_2 concentration. See Sections 3.2 and 3.6.3 for discussion of zero air supplies and the CO_2 interference effect.

4. Install the permeation tube or permeation device. Your commercial calibrator unit's operations manual will list the sizes and types of permeation devices which may be used. Before unpacking the permeation tube or device, have the calibrator and the clean air supply on and have a flow of air (about 100 cc/min or greater) passing through the permeation tube holder. Under dust-free and oil-free conditions, remove the permeation device from its shipping container in a ventilated area, preferably a fume hood. Immediately transfer the tube to the permeation holder of your calibrator and seal it in. If the permeation device has been stored under refrigeration, allow at least 24 hours equilibration time in the case of NBS tubes and longer times with other devices. Note that some manufacturers do not recommend storage of permeation devices at low temperature.

   It is most important to properly seal the permeation holder. If "O" rings or other sealing devices are used, be careful not to misalign them. Threaded Teflon parts must be tightened carefully to avoid leaks. Avoid stripping the threads. Teflon tape may be used to insure a good seal. Even a small leak in the permeation tube compartment will cause a dramatic change in concentration output since relatively high concentrations of SO_2 are present prior to dilution. Place the permeation tube (or tubes) in the holder in such a way that the tube does not obstruct entry or exit of sweep air.

5. Allow sufficient warmup time for oven and permeation device. Install the permeation device in its holder, set the temperature controller to the point recommended or desired for use with the permeation device, and allow the oven to warmup at least 12-14 hours; 24 hours is better. Allow the permeation tube or device to equilibrate 24 to 72 hours

depending on initial conditions and type of device. Maintain a flow of clean air through the permeation chamber during this time. Consult the manufacturer's literature for specific recommendations. Once the oven and permeation tube are equilibrated it is recommended that the system remain "on" or in "standby" and that air be flushed across the permeation device continuously.

The actual temperature of the operating permeation tube must be known with certainty. The calibrator should be equipped with an accurate (preferably NBS - traceable) temperature indicator of some kind - a thermometer, thermocouple or thermistor. Thermistors or thermocouples may be purchased and installed in most calibrators. Such devices may be purchased from Omega Engineering, Inc., Stamford, Conn., 06907.

6. Set and verify flows. The calibrator will have a needle valve or pressure regulator or perhaps a mass flow controller to control the diluent air flow. With rotameters, the position of the ball indicates the flow. By convention, scale readings are usually taken at the center of the ball. If your calibrator employs rotameters, a calibration curve will be provided by the manufacturer. This curve should have been established under or related to the normal conditions of 25° C and 760 mm Hg.

   When used to measure air flow rates, the main variable in rotameters is density. Assuming that the air is dry after passage through the filter and scrubber assembly, it is only necessary to correct the indicated flow for temperature and pressure effects.

   At an altitude of 1.5 km (5000 ft), a rotameter will read about 9% low as compared to sea level. A reading at 25° C instead of 0° C will cause the rotameter to read 5% low. Because the effects depend on a variety of factors, it is recommended that for precise work you prepare your own calibration curve. Use displacement techniques (soap film flowmeter, wet test meter, etc.) and correct for the effect of water vapor. These same techniques should be used to verify the flow rate on mass flowmeters and pressure regulator-orifice systems.

7. Interface the calibration system with the FPD SO_2 analyzer. Disconnect the FPD analyzer's Teflon ambient air sampling line from the station

ambient air sampling manifold and connect it to the calibration system's manifold. Be certain to supply excess sample flow through the calibration manifold to prevent dilution of the calibration gas by room air. About 500 cc/min excess (0.5 liters/min) is suggested as a minimum. Thus, if the instrument's sample flow rate is 250 cc/min, the overall flow from the calibrator should be at least 0.75 to 1.0 liter/min. Use only cleaned Teflon or glass materials to construct the calibration manifold. All excess calibration gas should be vented. Refer to Figures 3.6 and 3.7.

8. Provide zero air to the analyzer. By having the diluent air bypass the permeation tube compartment or by venting the permeation compartment contents, zero air is supplied to the analyzer. Allow sufficient time for a stable zero trace to be established. Set the analyzer to the desired zero point (refer to Section 4).

9. Provide span gas and intermediate concentrations of SO_2 to the analyzer. By adjusting the total flow (usually only the diluent air) different concentrations of SO_2 can be generated. The concentration of SO_2 at various flow rates can be computed from equations given in Section 3.4.4. Remember that the flows should be checked by displacement methods (soap film flowmeter or wet test meter) from time to time. Rotameters, pressure gauges, and mass flowmeters are subject to error and variation and need periodic verification. Also check the flow at the output of the calibration manifold to detect possible leaks in the calibration system.

   Always remember that SO_2 is a hazardous pollutant. Do not expose yourself to the calibration gas; do provide a well-ventilated work environment. All excess calibration gas should be vented. This may be done by connecting the calibration manifold to the station sampling manifold exhaust. Use large diameter tubing; avoid high vacuum exhausts.

10. Shutdown and maintenance. If the calibrator is shut down for any length of time, the permeation tube or device should be removed and stored in a desiccated container. The main areas for maintenance of calibrators are: replacement of scrubber materials (such as silica gel

and activated charcoal) on a time-of-use basis; cleanliness of valves and rotameters; verification of correct operation of heaters and temperature sensors; verification of correctness of flow and temperature measuring devices.

3.4.4 Computation of SO_2 Concentrations From Permeation Tubes

The output of a permeation tube or device is converted to concentration in parts per million (ppm) using the following equation:

$$C = \frac{(R)\ (MV)}{(F)\ (MW)}$$

where: C = Concentration in ppm by volume at 25° C and 1 atmosphere (760 mm Hg)

R = Permeation rate, micrograms/minute (μg/min)

MV = Molar volume (24.45 liters at standard conditions of 25° C and 760 mm Hg)

F = Total flow rate of air (purge air plus diluent air), liters/minute (at standard conditions of 25° C and 760 mm Hg)

MW = Molecular weight of the permeating gas (MW SO_2 = 64).

Example Calculation A - What is the ppm output of NBS permeation tube 33-64 (see Table 3.1) under the following calibration conditions?

Permeation tube oven temperature: 22.5° C

Purge air flow rate by soap film flow rate measurement: 180 cc/min

Dilution air flow rate by soap film flowmeter measurement: 4500 cc/min

Room air temperature: 28.0° C

Barometric pressure: 750 mm Hg

Step 1: determine the permeation rate, R, at 22.5° C using the equation given in Table 3.1.

$$\text{LOG } R = M(273.15 + t) - B$$

$$\text{LOG } R = 0.033759\ (273.15 + 22.5) - 9.97634$$

$$\text{LOG } R = 0.004508$$

From a table of five-place common logarithms:

ANTILOG of 0.004508 = 1.010 micrograms/minute = R

Step 2: determine the total air flow and correct it to the conditions 25° C and 760 mm Hg.

Total air flow = 180 + 4500 = 4680 cc/min

= 4.680 liters/minute

Apply this equation to convert the measured flow to the standard conditions of 25° C and 760 mm Hg pressure (refer to section 5.0 for an example):

$$F_s = F \times \frac{P - P'}{760} \times \frac{298.15}{t + 273.15}$$

where:

F_s = Flow rate at standard conditions in liters/minute

F = Measured total flow rate of air carrying SO_2 from the calibrator, liters/minute

P = Barometric pressure in mm Hg (inches of mercury may also be used provided 29.92 inches of mercury is used in the denominator, replacing 760 mm Hg)

P' = Vapor pressure of water, mm Hg (or inches Hg if P is measured in inches Hg) at temperature t (refer to table in section 5 or to a handbook of tables). This correction is made only when a soap film flowmeter or wet test meter is employed. Assuming the relative humidity of the metered air is 100%, this corrects for the vapor pressure of water.

t = Temperature of the calibration air in degrees C (or the room air temperature of the laboratory).

Thus:

$$F_s = 4.680 \times \frac{750 - 28.35}{760} \times \frac{298.15}{28.0 + 273.15}$$

$$F_s = 4.400 \text{ liters/minute}$$

Then:

$$C = \frac{(R)\,(MV)}{(F)\,(MW)}$$

$$C = \frac{(1.010)(24.45)}{(4.400)(64)} = \frac{(1.010\ \mu g/min)(24.45\ \mu l/\mu mole)}{(4.400\ l/min)(64\ \mu g/\mu mole)}$$

$$C = 0.088\ \mu l/l \quad \text{or} \quad 0.088\ \text{ppm}$$

Example Calculation B - What is the concentration of SO_2 expressed as micrograms/standard cubic meter ($\mu g/sm^3$) at the conditions given in Example Calculation A?

Use this equation: $C_m = \frac{R}{F_s} \times 1000\ \text{l/m}^3$

where:

C_m = Concentration, $\mu g/sm^3$

Thus:

$$C_m = \frac{1.010\ \mu g/\text{minute}}{4.400\ \text{liters/minute}} \times 1000\ \text{l/sm}^3 = 229.5\ \mu g/sm^3$$

$$C_m = 229.5\ \mu g/sm^3$$

Or, since 1 ppm SO_2 = 2615 $\mu g/m^3$ at normal temperature and pressure (25° C, 760 mm Hg), then:

$$0.088\ \text{ppm} \times 2615\ \mu g/m^3 = 230\ \mu g/m^3$$

3.5 CALIBRATION BY USE OF COMPRESSED GAS CYLINDERS CONTAINING SO_2 IN NITROGEN OR AIR

3.5.1 General

At present, the permeation tube is the most reliable and accurate source of SO_2 calibration gas. However, recent advances in compressed gas technology have made available special treated cylinders of SO_2 in air or nitrogen at high (50-500 ppm) or low (<1-10 ppm) concentrations. For example, the National Bureau of Standards has produced four primary standard SO_2 in N_2 mixtures intended for use in the calibration of instruments used in the analysis of sulfur dioxide in stack gases. These mixtures have been shown to be stable for long periods of time (certified for one year) when packaged in treated aluminum cylinders. Because the NBS Standard Reference Materials mentioned above are at high concentration levels (480 to 2521 ppm) and are diluted by nitrogen instead of air, they are not useful for calibration of ambient air FPD analyzers. NBS is, however, studying the stability of cylinders containing lower (50 ppm or less) concentrations of SO_2 in air. This study may result in a new Standard Reference Material.

Today, several specialty gas producers supply mixtures of SO_2 in air at concentrations ranging down to ambient levels. The higher level mixtures (100 ppm) have been found to be quite stable,[20,21] and can be diluted with clean air to ambient levels for use. Cylinders of 10 ppm (or less) SO_2 in air have also exhibited temperature and pressure stability with no appreciable decay in mixture concentration in one study.[20] However, recent field use of similar mixtures has revealed that low levels of SO_2 in air (usually below 50 ppm) in cylinders are not always stable and tend to decay in a short period of time.[22] This decay is illustrated in Figure 3.8.

Due to such concentration uncertainties, cylinders containing very low, ambient level SO_2 concentrations in air (i.e., less than 50 ppm) are not recommended for general calibration use at this time. They are useful for audits if standardized prior to and after field use and an accounting is made of any decay in concentration. The higher concentration SO_2 in air cylinders (50-100 ppm and greater) are useful for calibrations and audits and a list of good practices and procedures for their use is given below. It is recommended that the cylinder's concentration be established by comparison to an NBS SO_2 permeation tube system (i.e., establish traceability).

3.5.2 Equipment Specifications and Use

SO_2 Cylinder. At the present time, the most stable mixtures of SO_2 in air or nitrogen have been prepared in treated aluminum cylinders. Conventional steel cylinders are not acceptable. CGA valve outlets vary. NBS treated aluminum cylinders have CGA 350 outlets; other tanks have CGA 330 or 660 valve outlets.

Cylinders may be shipped and stored in the same way as any other which contains a toxic gas. If the cylinder has been shipped or stored under temperature conditions very much different from those inside the laboratory or air monitoring station where it will be used, an equilibration step is required. The cylinder is placed in the laboratory or station at least 24 to 48 hours prior to use. It is a good idea to let the cylinder, the attached regulator, and any dilution assemblies equilibrate in the sampling station at least overnight, under even the best of conditions.

Regulator for SO_2 Cylinder. The regulator should be a high purity, corrosion-resistant, stainless steel model with the correct CGA fitting. Further specifications are:

- Diaphragm constructed of type 316 stainless steel or other noncorroding metal; seals and seats of Teflon or Kel-F.

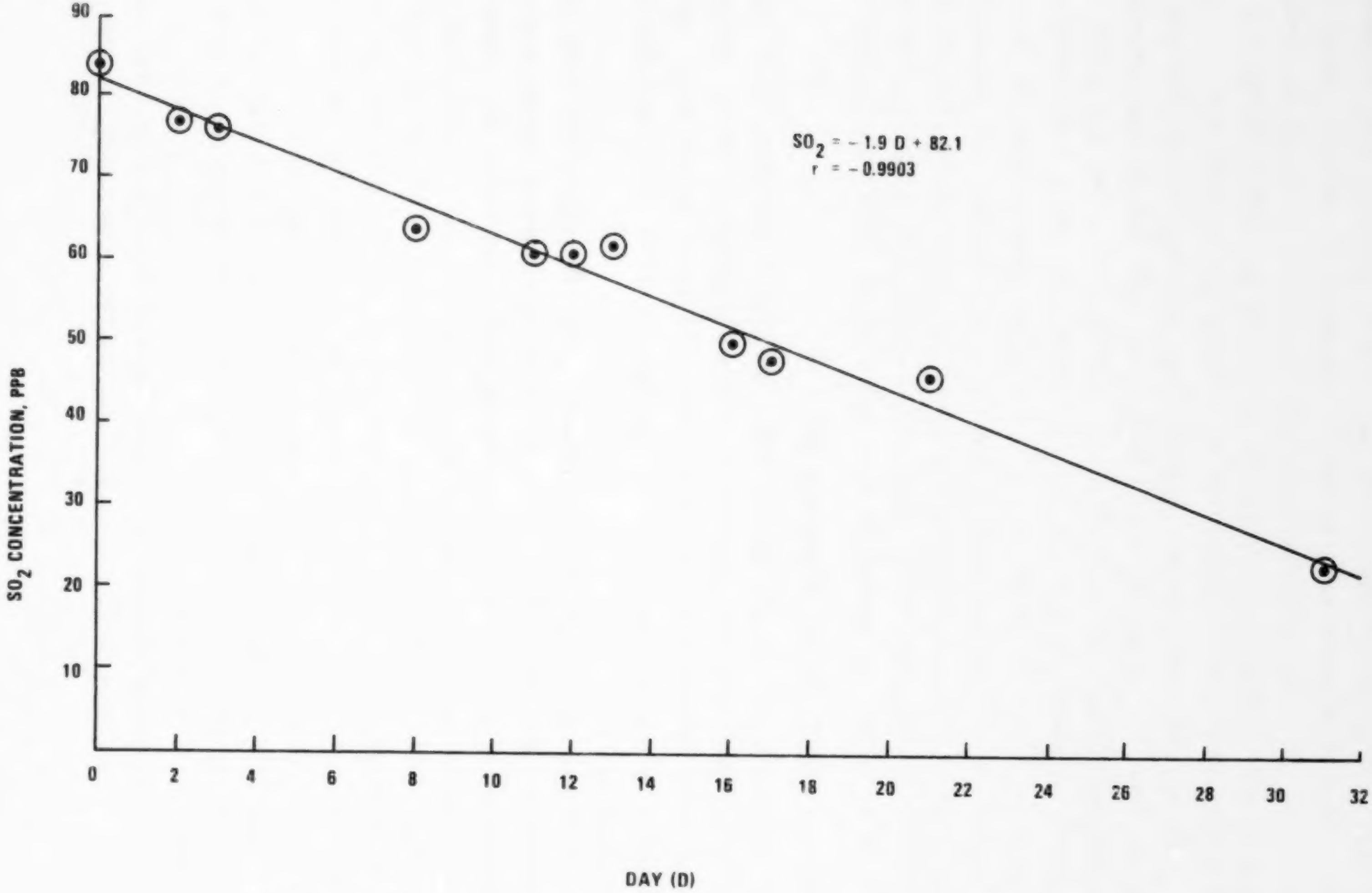


Figure 3.8. Concentration of SO_2 versus time. Low-level SO_2 in air; treated aluminum cylinder.[22]

- Two stage regulator preferred over one stage.
- Pressure gauges should be as small as possible with ranges of 0 to 3000 and -30 to 100 psig.
- Regulator should be equipped with a purge assembly option. The diaphragm of the regulator should be fully supported to permit evacuation of the regulator without damage to the diaphragm.

Examples of acceptable regulators include Matheson's Series 3800 two stage stainless steel regulator, Airco's Model 52 and Model 57 series, and Linde's Model UP-G. Other manufacturers offer similar equipment. This regulator should be dedicated for use only with SO_2 mixtures. Furthermore, an individual regulator should be used only with cylinders of approximately the same concentrations. For example, a regulator used to deliver 100 ppm concentrations should not be used to deliver much higher levels (such as 2500 ppm). To do so may cause a buildup of SO_2 on internal regulator parts which would require lengthy purging prior to re-use with lower concentration cylinders.

Dilution Assembly and Clean Air Source. Many commercial units are available which can dilute a small flow of SO_2 with clean air. A system may also be built. Such systems may employ limiting orifices or capillary networks to achieve a steady, low flow of SO_2. Passage of SO_2 mixtures through a rotameter is not recommended because SO_2 may be removed on its surfaces.

The air supplied to the dilution assembly should be regulated so that a series of known flow rates can be obtained. This is accomplished with needle valves, critical orifices, capillary tubes, or a mass flow controller. Clean air supplied to a flame photometric detector should contain ambient levels of CO_2.

The flow rates of both the SO_2 and the clean air should be determined with a calibrated soap film flowmeter or other calibrated meter. The final concentration is established based on the corrected flow rates.

Assembly of Components. Figure 3.9 shows a suggested layout for assembly of the cylinder, clean air supply, mixing devices and manifold. The arrangement is quite similar to that employed in permeation tube systems.

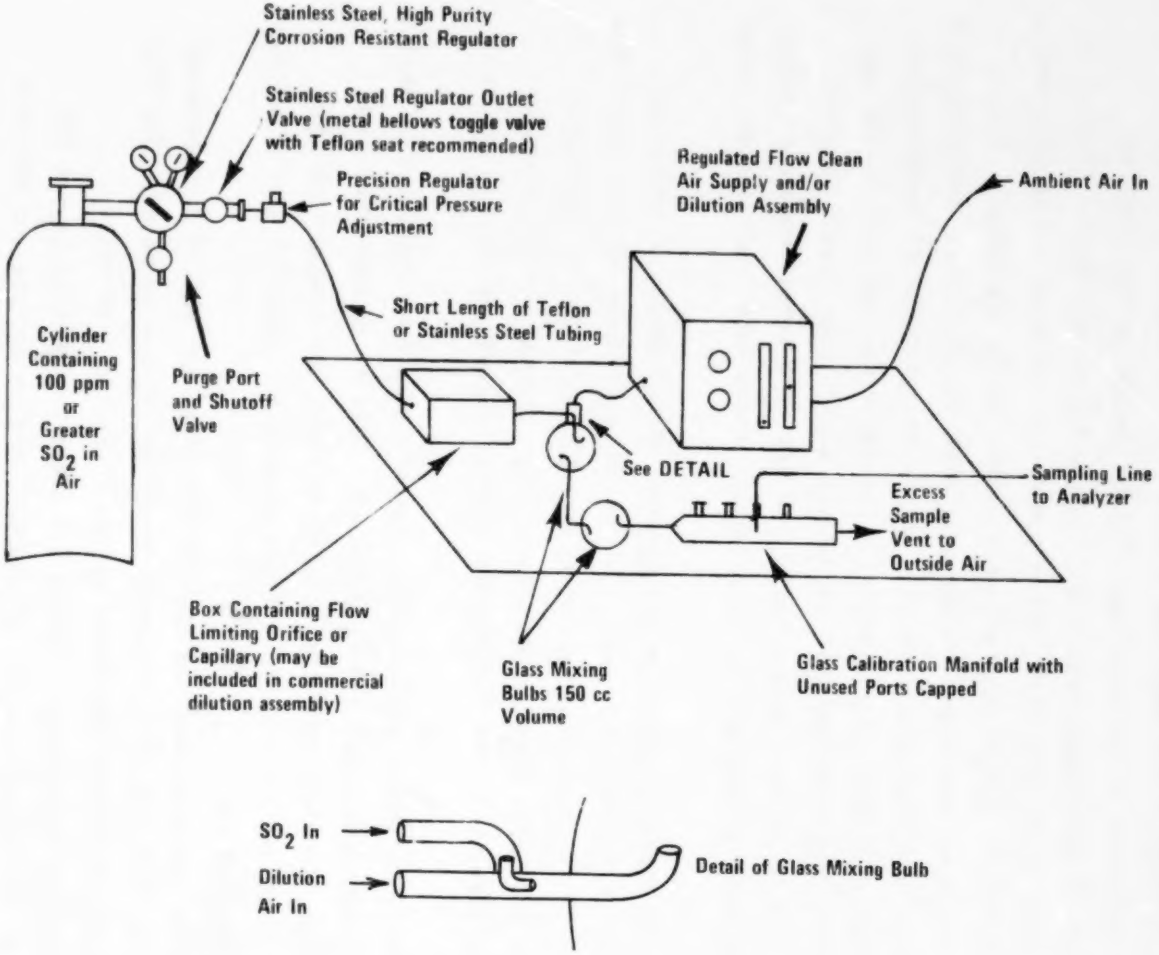

Stainless Steel, High Purity Corrosion Resistant Regulator
Stainless Steel Regulator Outlet Valve (metal bellows toggle valve with Teflon seat recommended)
Precision Regulator for Critical Pressure Adjustment
Regulated Flow Clean Air Supply and/or Dilution Assembly
Ambient Air In
Cylinder Containing 100 ppm or Greater SO2 in Air
Purge Port and Shutoff Valve
Short Length of Teflon or Stainless Steel Tubing
See DETAIL
Sampling Line to Analyzer
Excess Sample Vent to Outside Air
Box Containing Flow Limiting Orifice or Capillary (may be included in commercial dilution assembly)
Glass Mixing Bulbs 150 cc Volume
Glass Calibration Manifold with Unused Ports Capped
SO2 In
Dilution Air In
Detail of Glass Mixing Bulb

Figure 3.9. Assembly for dilution of SO_2 from cylinder for use in calibration or span check.

3.5.3 Guidelines for Use of SO_2 Dilution Systems

1. Allow the cylinder, attached regulator, and dilution assembly to equilibrate in the laboratory for 24-48 hours prior to use so that temperature equilibrium is reached.
2. During this equilibrium period, the tank's regulator should be thoroughly flushed and conditioned with SO_2. It is important to remove any gaseous or surface adhering water from the internal parts to avoid SO_2 removal. If the regulator is "wet," its effect on SO_2 concentration will be noted by a slowly increasing signal response on the continuous SO_2 analyzer. To expedite the removal of water, the purge assembly of the regulator is used in one or both of the following ways.
   a. Pressurization/Evacuation
      (1) Attach a small vacuum pump to the purge assembly fitting. Close the purge assembly valve. Close the regulator outlet valve.
      (2) Open the cylinder valve and pressurize the regulator. Adjust the regulator control valve to pressurize the low pressure gauge. Close the cylinder valve.
      (3) Turn on the pump, open the purge assembly valve and pull a vacuum on the regulator for 1 minute. The low pressure gauge should read a negative value. Close the purge assembly valve.
      (4) Repeat the pressurization/evacuation procedure 4 or 5 times. Remove the pump, and pressurize the regulator with the SO_2 mixture. Close the cylinder valve until ready for use.
   b. Purge with dry air or nitrogen
      Attach a cylinder of clean, very dry, nitrogen or air to the purge port. Open the purge port valve and regulator outlet valve. Allow a low flow of gas to purge through the regulator for 20-30 minutes.

After the regulator has been purged and conditioned, it should be left attached to the SO_2 cylinder, and filled with the SO_2 mixture. If it must be removed, the regulator may be protected from moisture by immediately capping or plugging the CGA outlet and closing all valves.

3. The concentration of a new cylinder of SO_2 in air (or nitrogen) should be re-established prior to actual field use by comparing its outlet to that of a permeation type calibration system whose permeation tube or device is an NBS Standard Reference Material or is traceable to an NBS permeation tube. An experienced person should conduct or oversee this operation.

   This is done by first calibrating a continuous SO_2 analyzer with a permeation tube system. Next the diluted gas from the SO_2 cylinder is sampled by the analyzer and, after stabilization of the signal, the concentration value is recorded. If a FPD analyzer is used, the air supplied to the permeation tube calibrator and the dilution assembly must have the same CO_2 content as the outside ambient air. Since the dilution factor is known, the tank concentration can be calculated and compared to the manufacturer's analysis. If the value so obtained is significantly lower than that stated on the cylinder, first check the dilution system for leaks or interferences to SO_2 detectability. If no fault is found, it is probable that the tank SO_2 level has decayed.

Example calculation:

F_1, SO_2 flow rate from tank: 10 cc/minute
F_2, Dilution air flow rate: 1420 cc/min
R, Calibrated analyzer response: 0.42 ppm

Thus:

$$[SO_2], \text{ppm} = (R)\ \frac{F_1 + F_2}{F_1}$$

$$[SO_2], \text{ppm} = (0.42)\ \frac{1420 + 10}{10}$$

$$[SO_2], \text{ppm (cylinder)} = 60.06$$

4. The cylinder may now be taken to ambient air monitoring stations for use as a calibration, span check, or audit device. Dilution air at each station should be processed ambient air so that the diluent air contains ambient levels of CO_2 when FPD analyzers are calibrated.

   CAUTION. Allow sufficient time for temperature equilibration of the cylinder at each monitoring station.

The SO_2 tank is used for multipoint calibration in much the same way as the permeation tube. The dilution air flow is varied to give different concentrations of SO_2; when the SO_2 supply line is disconnected or vented, the dilution air serves as a source of zero air.

5. The concentration stability of such SO_2 cylinders should be checked from time to time by returning the cylinder to a central laboratory for redetermination of its concentration by comparison to an NBS permeation system. This should be done at least quarterly for long-term studies and monthly for shorter term efforts. Replace the tank when the pressure reaches 500 psig.

3.6 OTHER FACTORS AFFECTING THE SO_2 OUTPUT FROM DYNAMIC CALIBRATION SYSTEMS AND/OR THE RESPONSE OF FPD SO_2 ANALYZERS

3.6.1 Temperature at Which the Permeation Tube is Used

The temperature at which the permeation tube is used must be precisely known and controlled to within ±0.1° C of the value selected. Knowledge of the correct temperature is very important since the permeation rate of tubes increases (or decreases) in a logarithmic fashion with change in temperatures. Table 3.2 illustrates the errors that are introduced for a typical tube when the temperature is unknowingly varied from an assumed value of 25.0° C.

3.6.2 Air Flow Rate and Clean Air Supply

The rate of air flow (cc/minute or liters/minute) across the permeation device must be known. This is established by calibration of the dilution air flow rate with a soap film flowmeter, wet test meter, or an air mass flowmeter. Each of these measuring devices must itself have been recently calibrated and referenced to an NBS traceable standard of volume.[19] See Section 5 for a discussion of the use and calibration of air flow measuring devices. Many calibration systems split the clean air supply and send a small portion of the flow over the permeation device and a large portion to combine with the SO_2-laden air coming from the permeation tube compartment. The gases leaving the permeation tube compartment contain SO_2 at relatively high levels. A small change in the flow rate across the tube would not affect the final concentration significantly since it would be small compared to the total flow. However, a leak in the permeation tube compartment

Table 3.2. Typical errors due to temperature variation of an SO_2 permeation tube

Temperature °C	Permeation Rate μg/minute	Concentration at 760 mm, 25° C (Dilution at 12 liters/minute)		Error[†] Percent
		μg/m³	ppm	
25.0	2.62	218	0.083	0
25.1	2.64	220	0.084	1
25.5	2.72	227	0.087	4
26.0	2.83	236	0.090	8
27.0	3.06	255	0.097	17

[†] Assuming the operator thought the temperature was at 25.0°C and was attempting to obtain 0.083 ppm SO_2

or in the lines leading to the dilution air would cause a large decrease in the SO_2 concentration since SO_2 at high concentrations would be escaping.

Certain materials such as stainless steel, dirty surfaces, and non-Teflon filters usually cause a diminishment of SO_2 by adsorption or reaction. Use only glass or Teflon tubing and Teflon filters in your calibration system.

An essential part of the calibration system is its supply of clean, dry SO_2-free, zero air. This air must be like ambient air in two important respects: the oxygen and nitrogen content must be the same as ambient air, and the CO_2 content should be similar to that in ambient air (300-350 ppm). The oxygen/nitrogen ratio affects the flame of the FPD, and the presence of CO_2 in ambient air will depress the signal if CO_2 was not present in the calibration gas.

3.6.3 Carbon Dioxide Interference in the FPD Method for Sulfur Dioxide

3.6.3.1 Nature of the Problem

A problem often encountered with FPD analysis of SO_2 and associated calibration procedures is the negative span interference or "quenching" caused by ambient CO_2. The best solution to the problem, at present, is to provide ambient levels of CO_2 in the calibration gas.

That the problem exists is shown by the results of recent audits[23] conducted at various ambient air measuring facilities, Table 3.3.

Part of the variance in response to the audit concentrations can be attributed to factors other than CO_2 interference. However, quantitative examination of the audited calibration system's CO_2 output often revealed CO_2 concentrations much less than ambient levels. Minimization of the CO_2 interference depends on having ambient levels of CO_2 present in the calibration gas.

Carbon dioxide is naturally present in the ambient atmosphere at average concentrations of 300-350 ppm. There are variations with height, time of day and season.[24] Near sources of CO_2, concentration variations may be significantly greater than those of rural ambient air. For instance, at ground level, near a densely populated and heavily traveled area of a city, the levels of CO_2 in air would be higher than that in the countryside.

The CO_2 does not react with or remove the SO_2. Its effect on the signal is probably due to collisional quenching processes which inhibit the formation of the excited state S_2^* molecule or deactivate the excited state S_2^* molecule prior to chemiluminescent emission.

$$S_2^* + CO_2 \longrightarrow S_2 + CO_2 \quad \text{(without chemiluminescent emission)}$$

Overall, this results in an apparent lowering of the FPD SO_2 concentration output signal, i.e., a negative span interference.

Table 3.4 shows analyzer response results for a modern 1976 model ambient air SO_2 FPD analyzer. One set of data was established in the presence of ambient CO_2, ~350 ppm, the other in the absence of CO_2. Note that the percent response increase at different SO_2 concentration levels is about the same, 17%, when the CO_2 is removed.

All commercially available continuous FPD SO_2 analyzers show this CO_2 effect to varying extents (see Table 3.3). The effect is not observed in analyzers which chromatographically separate SO_2 from other atmospheric gases (e.g., CO_2).

Table 3.3. Evaluation of CO_2 interference in total sulfur measurements using FPD analyzers[23]

Instrument Brand	SO_2 Audit Concentration (ppb)	Measured TS Concentrations			% Change From 0 ppm CO_2 Measurement	
		0 ppm CO_2 (ppb)	360 ppm CO_2 (ppb)	750 ppm CO_2 (ppb)	360 ppm CO_2	750 ppm CO_2
A	50	51	41	34	-20%	-33%
	99	107	92	78	-14%	-17%
	151	180	149	129	-17%	-28%
A	51	49	41	34	-16%	-31%
	101	111	90	74	-19%	-33%
	150	170	142	119	-16%	-30%
B	59	53	49	44	-8%	-17%
	103	108	100	92	-7%	-15%
	150	148	142	135	-4%	-9%
B	59	53	50	48	-6%	-9%
	103	107	101	101	-6%	-6%
	150	149	145	140	-3%	-6%
C	50	45	46	46	+2%	+2%
	100	91	90	82	-1%	-10%
	150	138	135	114	-2%	-17%
C	65	61	58	53	-5%	-13%
	127	126	116	101	-8%	-20%
	188	190	174	150	-8%	-21%
D	50	46	44	43	-4%	-7%
	99	95	88	84	-7%	-12%
	149	149	135	126	-9%	-15%
D	49	40	38	35	-5%	-13%
	102	91	87	84	-4%	-8%
	151	146	132	131	-10%	-10%

Table 3.4. FPD analyzer response, ppm SO_2, in the presence and absence of carbon dioxide.

Perm tube Predicted SO_2, ppm	Instrument Response, Volts (CO_2 present/ CO_2 absent)	Calculated[†] SO_2, ppm (CO_2 present at 350 ppm)	Calculated[†] SO_2, ppm (CO_2 absent)	% Response Increase, (CO_2 absent)
0.0	0.0135/0.014	0.006	0.007	-
0.437	0.875/1.032	0.439	0.518	18.0
0.338	0.678/0.795	0.340	0.399	17.3
0.278	0.540/0.630	0.271	0.316	16.6
0.144	0.283/0.335	0.142	0.168	15.5
0.099	0.191/0.225	0.096	0.113	17.7
0.078	0.149/0.176	0.075	0.088	17.3

[†] Calculated based on least squares regression calibration equation established in the presence of ~350 ppm CO_2.

3.6.3.2 Minimization of the CO_2 Interference

The CO_2 interference can be minimized by dynamically calibrating the analyzer with SO_2 in air mixtures containing ambient levels of CO_2 (~350 ppm). Then, when the analyzer is returned to ambient air, it will "see" approximately the same amount of CO_2 and the effect will be the same as during calibration. In this way the CO_2 interference has been "nulled out" or compensated for by the calibration zero and span adjustments.

It should be noted that calibration and rechecks of calibration will not uncover the presence of a CO_2 interference. For instance, one might calibrate with air mixed with SO_2 containing no CO_2. The calibration may be repeated and give excellent agreement with the first calibration. However, when the analyzer is returned to ambient air, an immediate quenching of the SO_2 signal occurs.

Of course, if the concentration of CO_2 in the air used for calibration purposes changes dramatically from one calibration to the next, there can be a noticeable difference between successive calibration span values. This effect could be mistaken for instrument span drift or calibration gas inaccuracy.

To ensure that ambient levels of CO_2 are included in the calibration gases, a calibration system should be set up which uses on-site outside ambient air (which is scrubbed free of sulfur compounds but not CO_2) as a source of zero and dilution air.

Ambient air, taken from outside the sampling station, must be used and can be obtained from the station sampling manifold. Do not use room air. Room air CO_2 levels may be much higher than those of ambient air. If the analyzer is calibrated with air containing CO_2 levels higher than in ambient air, the response to SO_2 upon return to ambient air will be greater than during calibration, resulting in an apparent positive interference.

A zero air generator suitable for FPD zero and calibration work is shown in Figure 3.1, Section 3.2.1. A laboratory experiment was carried out to determine the amount of CO_2 which passes through commonly employed scrubbers. A 3.8 x 15 cm (1.5 x 6 inch) cylindrical column contained the scrubber material; flow rate of the air/CO_2 mixture through the system was 1 liter per minute. Analysis was by gas chromatography. Results are summarized in Table 3.5.

The results show that the SO_2-scrubbing agent, activated coconut charcoal, does not retain CO_2 significantly, especially if it is conditioned prior to use. The drying agents, "Drierite" (TM) and silica gel, pass CO_2 quantitatively. Molecular sieves (which are often found in heatless air dryers) completely remove CO_2 and should not be used. Soda lime and "Ascarite" (TM) also absorb CO_2 completely and should not be used as scrubber material.

Parameters for the operation of individual clean air systems should be optimized by the user. The dimensions of the scrubber cartridge and the amount of material packed inside will be dictated by the air flow rate, the length of time the system is used before repacking the scrubbers, and the concentration of pollutants present in the ambient air.

Most commercial calibration systems intended for use in calibrating ambient level FPD SO_2 monitors will normally have a nominal total air flow of from 2-5 liters/minute.

3.6.4 Percentage of Oxygen in Calibration Air

The flame photometric detector has been shown to give a varying response to SO_2 when air supplied to the flame has a varying oxygen content.

Table 3.5. Retention of CO_2 on commonly employed scrubber materials.

Scrubber material	CO_2, ppm prior to scrubber	CO_2, ppm after scrubber	Exposure time, minutes
Activated coconut charcoal, 6-14 mesh, taken directly from new container. 56g.	350	245	88
Activated coconut charcoal, 6-18 mesh, conditioned for 16.5 hrs. at 300°C in air. 56g.	350	345	80
"Drierite" (TM), 10-20 mesh. 20g.	350	347	32
Molecular sieves, Type 5A, 8-12 mesh. 28g.	350	0	32
Silica gel, indicating, coarse mesh. 67g.	350	350	150

The use of scrubbed ambient air for zero and dilution is recommended in order to avoid this problem. If cylinder air is used, it should contain the correct ambient percentage of oxygen (20.94) and nitrogen (78.9). Heatless air dryers may also slightly alter the oxygen content of ambient air.

Figure 3.10 illustrates the variation in response of an FPD analyzer to a fixed concentration of SO_2 diluted by air of varying oxygen content.

3.7 SUMMARY OF FPD SO_2 CALIBRATION SOURCE PARAMETERS WHICH MUST BE OPERATOR-CONTROLLED

Table 3.6 presents a checklist of calibration source parameters which must be operator-controlled in order to obtain valid data from FPD SO_2

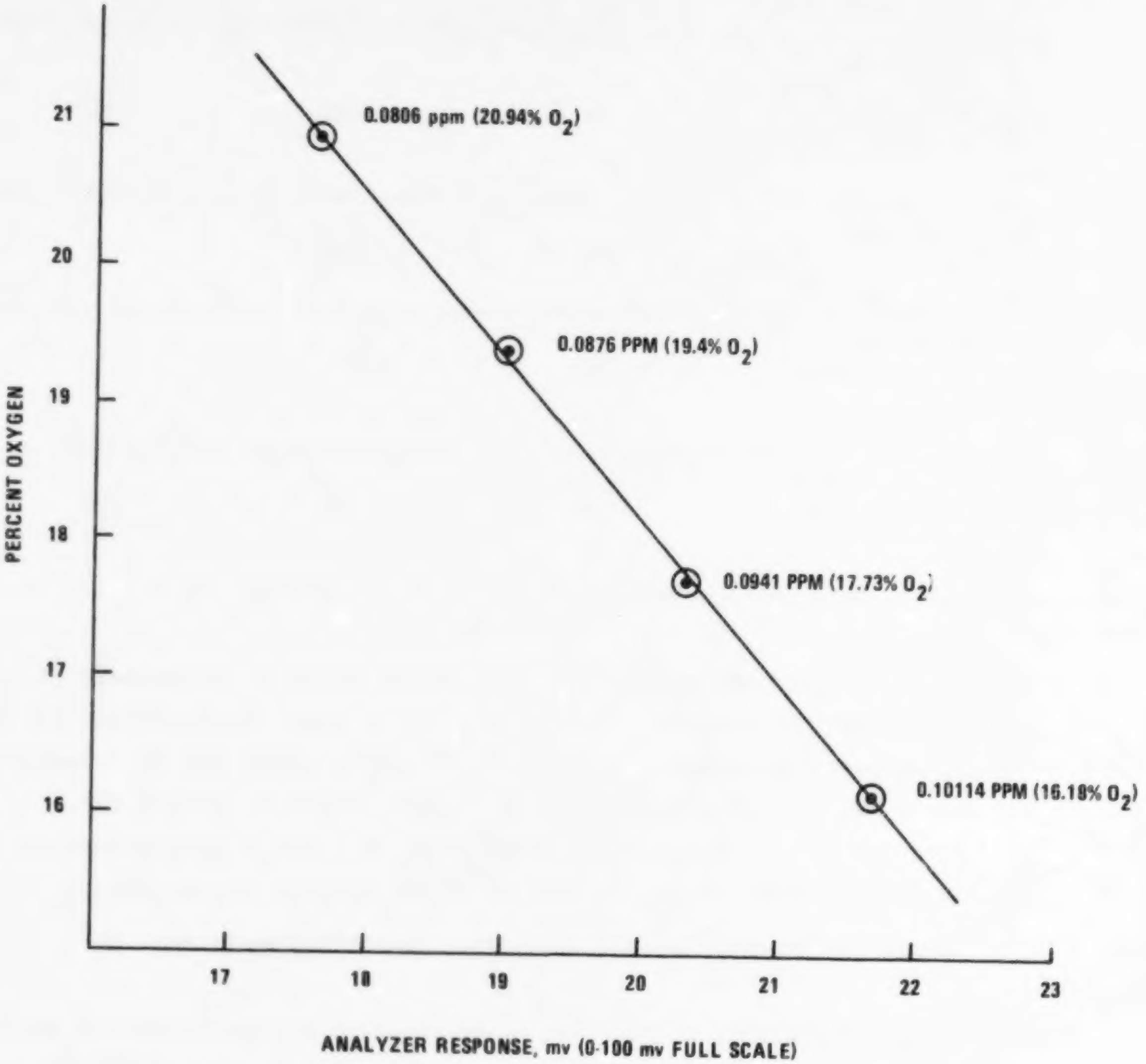


Figure 3.10. Variation of FPD analyzer response with air oxygen content at a fixed SO_2 concentration of 0.0806 ppm.

analyzers. The table lists the parameter, how the operator controls the parameter, how lack of control can be identified, and how the parameter may be brought into control.

Table 3.6. SO_2 calibration source parameters which must be operator-controlled in order to obtain valid data

PARAMETER

Knowledge of the permeation rate of SO_2 from tube or device

How Operator Controls Parameter

1. Purchase NBS certified SO_2 permeation tubes; use as received or employ for establishing traceability of other tubes or devices.
2. Purchase other tubes or devices which:
    a. Are certified by their manufacturer as being calibrated by use of NBS or NBS-traceable materials.
    b. Can be compared to SO_2 standard atmospheres generated in your laboratory by use of NBS permeation tubes.
3. Exercise care in storage, handling, and use of permeation tubes.

How Operator May Identify Lack of Control

The expected output of the tube or device changes with time and no other factor can be identified (temperature, flow, etc.) which could cause the problem.

The outlet from the tube or device does not agree with the expected value when the calibration system is compared to another system which uses an NBS certified tube.

The tube contains no visible liquid SO_2 or is visibly cracked or split, or is visibly oily or dirty.

How Operator May Bring Parameter Into Control

A defective permeation tube cannot be repaired, it must be replaced.

Table 3.6. SO_2 calibration source parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Temperature of permeation tube bath or holder

How Operator Controls Parameter

Some commercial permeation tube or device type calibration systems have an adjustable dial or thumbwheel to set the temperature of the air bath or compartment which contains the permeation device. Other systems are preset at some temperature (such as 35°C) and cannot be adjusted. Temperatures in systems employing recirculating water (or other fluid) are set using controls of the constant temperature water bath.

How Operator May Identify Lack of Control

A small change in the temperature of the permeation tube will cause a change in the concentration of SO_2 produced. This is one indication of temperature variation. Also check the thermocouple signal output of the system for indication of drift. Some calibration sources have a meter which indicates whether temperatures are being controlled or not. Check it.

If it is possible to do so, a thermometer (of NBS or ASTM accuracy) with at least ±0.1°C graduations should be placed in the permeation tube compartment with the mercury bulb located next to the permeation tube while air is flowing across the permeation tube. A thermocouple or thermistor may also be used as a temperature sensor.

How Operator May Bring Parameter Into Control

If heating and cooling devices are unstable or defective, replace them and calibrate the temperature output with a thermometer or thermocouple/thermistor arrangement. If unable to calibrate temperatures, compare the system's SO_2 output to that of an independent SO_2 source which has been temperature calibrated and which uses NBS permeation tubes.

If a temperature-adjustable system is operating satisfactorily but is only out of calibration, make adjustments and recalibrate the system.

Table 3.6. SO_2 calibration source parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Flow rate of purge air and dilution air

How Operator Controls Parameter

Control is usually by use of resettable pressure regulators and/or rotameters which are coupled to restrictive capillaries and orifices. Such pressure settings and rotameter readings must be correlated with actual flow rate by flow calibration.

How Operator May Identify Lack of Control

An increase in total air flow will result in a decrease in SO_2 concentration.

A decrease in total air flow will result in an increase in SO_2 concentration.

How Operator May Bring Parameter Into Control

First, check the dial settings on the calibration system's pressure gauges and rotameters to be sure they are at the desired settings. If they are wrong, next check the pressure at the source of the air supply, tank or compressor. If too low, increase the tank pressure, replace the tank or correct the compressor problem. Be sure compression pumps are operating.

Second, check the calibration and analyzer system for leaks. Use leak detection solution on pressurized lines only.

If the pressure gauges or rotameters are simply misadjusted, reset them.

It is most important that no leaks occur in the permeation tube holder since SO_2 will be vented in large concentration. By use of a bubble flowmeter, this flow should be established and rechecked occasionally. This is done by breaking into the line downstream of the permeation holder. The dilution air flow settings (gauge or rotameter) must also be matched with actual air flow by calibration with a bubble flowmeter or wet test meter.

Two ways to check for system leaks are suggested: 1. measure flow at the inlet and outlet and compare; 2. plug the outlet and pressurize the system with air, then use leak detector solution.

Table 3.6. SO_2 calibration source parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Interferences to SO_2 concentration or response of FPD analyzer

The major problems are caused by:

1. Use of stainless steel tubing or other tubing besides Teflon or glass (causes loss of SO_2 and/or slow analyzer response).
2. Water condensation in zero and/or dilution air (causes loss of SO_2).
3. Wrong $O_2:N_2$ ratio in zero and dilution air (causes variability of flame and may increase or decrease response to SO_2).
4. Zero or less than ambient amounts of CO_2 in the zero and/or dilution air (causes an apparent diminishment in SO_2 concentration when analyzer is returned to ambient air).
5. Pressurization of the SO_2 calibration manifold.

How Operator Controls Parameter

1. Use only Teflon or glass to deliver SO_2 to analyzer.
2. Provide air free of condensation by use of scrubbers, or in the case of compressed ambient air, provide route for excess liquid water to escape from compression chamber.
3. Use SO_2-free ambient air where possible. If compressed cylinder air is used, specify that it be ambient compressed air. If synthetic air (prepared from $O_2 + N_2$)is used, request an analysis of contents. The desired concentrations are: 20.9% O_2, 78.9% N_2, and 350 ppm CO_2.
4. Use dry, SO_2-free ambient air where possible. Air supply system must be such that the ambient air CO_2 content is maintained. If compressed air from cylinders is used, ambient CO_2 levels (350 ppm) should be present. Analysis for CO_2 should be requested.
5. Provide restriction-free venting of the calibration manifold. If a vacuum is used at the vent, be certain it is a light, gentle vacuum which will not cause a partial vacuum to occur within the calibration manifold.

Table 3.6. SO_2 calibration source parameters which must be operator-controlled in order to obtain valid data (continued)

How Operator May Identify Lack of Control

1. Inspect tubing and fittings of calibration systems.
2. Moisture droplets appear in tubing. Moisture scrubber is exhausted. If an indicating drier is used (such as indicating Drierite or silica gel), the color will change from blue to pink as it becomes exhausted.
3. A sudden change occurs in instrument response to SO_2 (increase or decrease) immediately after attachment of a new source of zero air.
4. Chemically measure the amount of CO_2 in your zero air at the calibration manifold (see Section 5 for instructions).
5. Attach a water manometer pressure gauge to one of the calibration manifold outlets. No pressure or vacuum should register. Momentarily remove any vent lines, etc. and continue to sample a known SO_2 concentration with the FPD. If any change in response occurs, the presence of the vent tube, etc. must have been causing an effect.

How Operator May Bring Parameter Into Control

1. Replace all tubings, fittings with Teflon and/or glass material.
2. Provide vent or other route for excess water to escape from pressurization system. Add a water scrubber (such as Drierite or silica gel) to your zero air system; replace exhausted drying agent.
3. Specify that your zero air contain 20.9%, 78.9% N_2, 350 ppm CO_2.
4. Use a system which does not scrub CO_2 from ambient air if ambient air is scrubbed and used as a source of zero air. If compressed cylinder air is used, be sure CO_2 is part of the mixture (request analysis if necessary).
5. Remove any restrictions to proper venting of the calibration manifold. Use a light, gentle vacuum at the vent.

CONCLUDED

SECTION 4.0

CALIBRATION OF THE FLAME PHOTOMETRIC DETECTOR FOR SO_2 IN AMBIENT AIR

4.1 INTRODUCTION TO CALIBRATION

4.1.1 Qualitative and Quantitative Analyses

The qualitative basis for any analytical method is the occurrence of a change in some property of the analytical system when the compound you wish to determine is added.

The flame photometric detection of SO_2 is a qualitative procedure. When SO_2 reaches the H_2/air flame, processes occur which produce an excited-state S_2 molecule. This molecule loses its excess energy by emitting light, and this light is sensed by a photomultiplier tube. The amperage signal from the photomultiplier tube is converted electronically to a voltage signal, which is displayed on a voltmeter or a stripchart recorder.

It is understood that the analytical method must be specific for the compound being determined. This is another way of saying the analytical method for compound A has no positive or negative interferences from compounds B, C, D, etc. However, in practice, most analytical methods suffer interferences. Without modification, flame photometry is not specific for SO_2 detection. When burned in a hydrogen-rich flame, any sulfur-containing gas may produce the excited-state S_2 molecule, which decays and emits light with a range of wavelengths centering around 394 nm. To be certain that the light of other wavelengths does not reach the photomultiplier tube, a 394-nm narrow band pass optical filter is used. This makes the FPD highly selective for detection of sulfur-containing compounds. In a further step, the FPD is made highly specific for SO_2 by the use of a "scrubber," which removes H_2S from the sample air stream while allowing SO_2 to pass unaffected. A chromatography column can also separate SO_2 from unwanted compounds.

A qualitative analysis can become a quantitative analysis. A quantitative analysis is one which not only tells you what compound, but also how much of that compound is present. To assign a value to an unknown concentration, the change or response of the analytical system to the unknown is compared to predetermined responses obtained for a sample containing none of the compound (known as a blank or zero) and a series of samples of known concentration. The concentrations which are known have been previously established by another analytical method. This set of known concentrations is sometimes called a set of standards. The process of obtaining the analytical system's responses for the members of a set of standards is often called standardization of the analytical method. Another term describing this process is calibration.

4.1.2 Definition of Calibration; Requirements for Calibration

In general terms, calibration is the process of precisely relating the magnitude (size) of the response of the analytical system to the concentration of the compound being measured. To achieve a valid calibration, two major requirements must be met.

1. The response of the analytical method to different concentrations of standard should be as reproducible and unvarying as possible. This is achieved by careful control of parameters affecting response. Furthermore, the effects of any interferences on response must be accounted for.
2. The concentration of the compound used as a standard for calibration must be known with a high degree of accuracy. This degree of accuracy must be within the limits of sensitivity of the analytical method. The standards must be sampled by the analytical method in the same way that unknown samples are taken.

To meet these two major requirements, careful control of parameters affecting the calibration standards (discussed in Section 3.0) and the analytical method (discussed in this section) must be maintained.

The meaning of the word "calibration" as applied to an automated analyzer such as the FPD SO_2 must be clearly understood. Calibration for automated methods refers to a complete multipoint characterization of the analyzer's response to an accurate, reliable standard over the entire analyzer range. A "zero and span operation" consists of a baseline check with clean air and a one-point check of analyzer response. Zero and span is not an acceptable basis for calibration.

An FPD SO_2 analyzer should be calibrated on-site upon installation and at intervals thereafter. Monthly calibrations are suggested; calibration every 2 weeks may be best in some cases. Zero and span checks should be performed more frequently--daily if possible. These procedures, along with maintenance and preventive maintenance are important parts of an air-monitoring system's quality control program and are essential in maintaining the accuracy and reliability of air quality data.

It is important that the FPD analyzer be operated during calibration under conditions identical to those in its normal ambient air sampling mode of operation. No modifications or alterations should be made to the analyzer's components, flow system, prescribed flow rate, or other parameters. Concentrations of SO_2 intended for calibration must be generated continuously by means entirely independent of the analyzer. The flow rate of the calibration gas must exceed the sample flow rate of the analyzer. The calibration gas should flow through a manifold and the analyzer should draw its sample through the regular ambient air sampling line, which is attached to a port of the vented calibration manifold.

This section of the TAD covers more than just a procedure for multipoint calibration of an FPD analyzer. Also included are suggested steps for station maintenance and recordkeeping, how to conduct a zero and span check, a short section on maintenance and replacement operations, and a checklist of FPD analyzer parameters and their control.

The procedure for multipoint calibration of an FPD analyzer is necessarily general. Where analyzer-specific instructions or explanations are necessary, the reader is referred to supplementary information located at the end of the procedure and to the manufacturer's instruction manual.

Special explanatory and precautionary material in the text is set apart by being enclosed in blocks.

4.1.3. Recordkeeping

A permanent record should be kept on all activities relating to calibration and maintenance of the FPD analyzer. The date and time intervals should be clearly noted. Also keep records on such items as: maintenance of calibration devices, calibration gases, hydrogen supplies, other analyzers, and the monitoring station itself. Also, record your name in the notebook, on the stripchart, etc.

A hardbound laboratory notebook is highly recommended. Make legible entries in ink; cross through erroneous entries with a single line. Many users find calibration and maintenance forms useful since they remind the operator to perform certain steps. If such forms are used, a copy should be pasted or taped into the notebook along with calibration curves and equations.

The stripchart record should also be marked. A short description of the action taken should be given. Times should be noted and marked clearly with a line or arrow.

4.2 PRELIMINARY STEPS

Before calibrating the FPD SO_2 analyzer, certain preliminary steps are taken. All of these steps are carried out before any adjustments are made to the analyzer, the calibration system, the data recording system, or other laboratory equipment serving the analyzer. In this way, any changes that have occurred in the total analytical system since the last calibration or check can be recognized and recorded. By examining this record over a period of time, problems of the analyzer (such as varying sample flow rate), the calibrator (such as temperature drift), or the station environment (such as inadequate temperature control) can be recognized and corrected.

1. Survey station condition. Check temperature/humidity control, cleanliness of station ambient air inlet, etc. Record findings in station logbook.
2. FPD Analyzer online, warmed up. Before calibrating an FPD analyzer, the electronics and flame should have been on (sampling mode) for at least 24 hours.

> If this is an initial calibration of a new instrument, a good practice is to test the analyzer for 5 to 7 days while conducting an accelerated program of zero, span, and multipoint calibrations. In other words, during this first week, calibrate the instrument about three times and carefully compare results from one calibration to the next to detect sources of error or drift, which need correction prior to recording ambient air data.

3. Calibration system online, warmed up. If a calibration system employing a permeation tube or device is to be used, the following steps must be completed before calibration begins:

a. The permeation tube or device must have been installed in its compartment and the constant temperature air or water bath must have been in operation at the desired temperature for at least 24 to 48 hours if the tube or device is initially at a temperature 10° C different from that of the oven. If its temperature is only 1° or 2° C different from that of the oven, 3 hours of equilibration time may be adequate. Shorter or longer times may be required and these times can only be deduced by experience. During equilibration a low flow of clean air (sweep air) must pass over the permeation device. Without this air flow, large concentrations of SO_2 will build up in the permeation compartment and lengthy purging with clean air will be necessary.

b. The source of clean, SO_2-free air (used for zero air, sweep air, and diluent air) must be in a state of readiness. If heated scrubbers (such as catalytic oxidizers) are used, such devices should be powered, warmed up, and producing clean air prior to use with the calibrator. Spent cartridges of chemical scrubbers should be replaced with equivalent materials, dirty filters should be replaced and conditioned, and water condensation traps should be emptied. Dirty or sticking rotameters should be disassembled and cleaned, dried, reassembled, and recalibrated. It is easier to perform such maintenance in the central laboratory rather than at the field site. Record all maintenance activities in the station logbook or in a notebook devoted to the calibration system.

NOTE: Following any maintenance or replacement activities on the calibration system, it is important to:

(1) Double check all connections for air leaks.

(2) Check the zero air output from the system to be certain that the new chemical scrubbers are not off-gasing any sulfur-containing compounds. In other words,

does the FPD signal increase dramatically on "zero" air after the scrubbers are replaced? If it does, the scrubber packing or holder is contaminated and must be replaced.

(3) Compare the instrument response to the zero air produced by the new scrubber system with the response to zero air from the previous scrubber system. If the response is significantly lower for the new scrubber than for the old, this indicates that the old scrubber system was exhausted and was allowing SO_2 to pass. Record any significant variations and make a report to the data validation section since some prior data may need to be voided.

(4) Be certain that the flow rates of zero, sweep, and diluent air have not been altered. Redetermine flow rates if necessary.

c. The relation between the settings of rotameters or pressure dials of the calibration system and the flow rate of dilution air and permeation tube sweep air should be established by calibration of the air flow with a wet-test meter or soap film flowmeter. See Section 5 for an explanation of the use of these devices. All measured flow rates should be corrected to standard temperature and pressure conditions, 25° C, 760 mm Hg. See Section 5 for the procedure for correcting air flow rates to STP.

d. If the permeation tube has not been used for some time, examine it visually to be sure liquid SO_2 is still present. Order calibrated permeation tubes or devices in plenty of time to provide replacement. As long as 4 months may be required to receive an NBS-certified permeation tube. See Section 3 for information concerning permeation tubes and devices.

e. It is very important to verify that the permeation tube oven temperature is correct. Any indicator dials or thermometers present should be examined often for signs of temperature drift. The use of thermistors or certified thermometers to check or verify the temperature as part of a preventive maintenance schedule is recommended.

4. Observe and record in the notebook all operational functions of the FPD analyzer. Make no adjustments at this time. If values are "off," they will be corrected later in the calibration procedure. Record:

   a. Sample flow rate. Activate the sample flow rate rotameter and record the center of the ball reading. The sampling rate may also be measured by removing the instrument sample line from the ambient air manifold, attaching it to a soap film flowmeter, and calculating the flow rate.

   b. Hydrogen fuel flow rate. Record the center of the ball reading for the hydrogen rotameter. Check the hydrogen pressure as indicated by the pressure gauge at the analyzer and the gauge at the hydrogen tank or generator.

   c. If desired, check and record the temperatures of the analyzer's photomultiplier tube oven, burner block, and exhaust line. This is done by attaching a thermocouple readout device to output jacks, which are generally located on the rear panel of the analyzer.

> NOTE: If the FPD analyzer flame is out, it must, of course, be relighted. It may be necessary to adjust fuel and air flow rates or perform maintenance to achieve ignition. Note your actions in the logbook. Wait for a stable zero or span signal to occur before proceeding to the multipoint calibration.

5. Check the stripchart recorder and/or data acquisition system. First, mark and note clearly on the recorder paper the time, date, and a brief description of your actions.

a. Determine any time discrepancy between the recorder and the local time. Over a period of days, the recorder drive mechanism may lag behind or speed up with respect to local time. This could be due to power failure, an inaccurate chart drive mechanism, or to binding, or slippage of the chart paper on the drive mechanism. Note the time discrepancy in the station logbook, determine its cause, and take corrective action.

b. Remove the stripchart roll and examine the ambient air trace (and any automatic zero or span checks) for the previous 24 hours. Look for evidence of power failure, flameout and automatic reignition, unusually high values, unusually low values (such as a straight zero baseline), and noisy signals.

> Such information is helpful in determining the present status of the analyzer and will indicate whether further warmup time is necessary before calibration. The stripchart roll should be clearly marked with the station number and inclusive times and dates and forwarded to the person responsible for data analysis.

c. Check the ink supply of the recorder. Add ink and clean the system as necessary. Replace the stripchart roll with a new one. Move the paper and start the pen at the desired time mark, and record the station name, date, and time on the stripchart.

d. If a data acquisition system (DAS) is being used, remove the magnetic tape cartridge and insert a new one. Some operators may prefer to leave the old tape in place, recording data, until the multipoint calibration is complete. Others may prefer to have the new calibration data entered on the new tape. If the calibration data are entered on the new tape, later application of the calibration equation to the raw data points acquired during calibration should give the correct calibration values if the scan or integrating interval of the

DAS is short enough. This serves as a check on the integrity of the data acquisition system and the computer program, which treats the raw data.

> Always take adequate notes of time on, time off, any analyzer response scale changes made, periods of calibration, etc. See that these notes reach the person responsible for magnetic tape data workup and interpretation so that signal variations due to calibration, zero, span, power failures, etc., are recognized and not confused with ambient air data.

6. Connect the stripchart recorder to analyzer. If a recorder is not already in place, connect one to the analyzer. Be sure the range of the recorder matches that of the analyzer output. It is recommended that the recorder baseline be offset to create a live zero for instruments having both positive and negative signal output. This is done by calibrating the recorder so a zero voltage input corresponds to 5 percent of the full-scale chart (i.e., 5 chart divisions if the paper has 100 divisions). A digital voltmeter may also be connected at this time. This will also permit the identification of negative zero drifts during calibration.

> A good practice is to use shielded cables to make signal connections. Consult the recorder manufacturer's manual for instructions. Since the recorder trace is often used as the permanent record for the data, the operator must be aware of the potential for error by problems such as:
>
> a. Recorder "dead band" error,
> b. Noisy trace due to improper gain adjustment,
> c. Loading error caused by the recorder and/or the voltmeter, and
> d. Erroneously set zero and span points.

Recorders and voltmeters should be carefully checked and calibrated to avoid such errors. Refer any questions or problems to an experienced electronics technician. Records should be kept of recorder and voltmeter calibrations and adjustments or repairs. Preventive maintenance programs should include recorders, data acquisition systems, and electronic measurement devices.

7. Obtain station temperature and pressure. In order to correct any measured volumetric flow rates to standard temperature (25° C) and pressure (760 mm Hg or 29.92 in. Hg), the temperature of the calibration air sample and the barometric pressure at the site must be known.

The temperature of the calibration gas is best determined by inserting a precision-grade glass thermometer into the calibration manifold. Once a steady temperature is attained, record the value and remove the thermometer. The room air temperature of the station may also be used, but it is possibly a less accurate reading than that taken directly from the manifold.

The atmospheric pressure is best obtained by reading a mercury column barometer or aneroid barometer which is located in the sampling station and has been in place long enough to achieve temperature equilibrium. Refer to Section 5 for instruction in the use and reading of barometers.

The nearest airport that maintains atmospheric pressure data may be called for information. Be sure that you ask for the actual "station pressure," not the pressure used by aviators, which has been corrected to sea level.

EXAMPLE. A call was placed to the local airport weather service on March 22. The recorded announcement stated the pressure was 29.60 in. Hg at 2:00 p.m. This is the value for aviators.

According to the meterologist on duty, the actual station pressure at 2:00 p.m. was 29.185 in. Hg. This latter value is the one to be used in volumetric correction equations.

The pressure at a site may be approximated by reference to a table listing barometric pressure at various altitudes. The elevation of the site must be known. See Table 4.1.

> EXAMPLE. An ambient air sampling station is located at an altitude of 2,058 feet above sea level. What is the average pressure at the site in mm Hg?
>
> From Table 4.1, $P_{site} = 27.70 + .02 = 27.72$ in. Hg
>
> (25.4 mm/inch) (27.72 in. Hg) = 704 mm Hg.

Be aware that significant temperature and pressure changes can occur during the timeframe of a calibration. If a barometer is present in the station, a reading should also be recorded at the conclusion of the calibration. A significant change may explain minor variations in instrument response since the instrument sampling rate is not mass-flow controlled.

4.3 ZERO AND SPAN CHECK

A zero and span check consists of a determination of an analyzer's baseline response to clean air and to a single SO_2 span point. In this way, certain analyzer malfunctions and drift that occur between calibrations may be detected. A zero and span check should be conducted daily if possible and just prior to a multipoint calibration. Only slight adjustments should be made to the zero pot; no adjustments should be made to the span pot. A zero and span check should not be confused with a multipoint calibration. Zero and span data should not be used as a basis for data workup. Zero and span data are very useful to help an operator keep track of daily zero and span drifts. In contrast to a multipoint calibration, a zero and span check uses only two points and perhaps uses a less accurate, less reliable, or nondynamic SO_2 standard.

Often a zero air source is included within the analyzer. Zero air is supplied by having the analyzer's sample pump pull air through a charcoal-filled cartridge. By activating a solenoid valve, the air sample is pulled through the cartridge rather than through the ambient air sample line. Thus, the path of the built-in zero air is not the same as that followed by ambient air. The span gas may also enter by a path other than that used for

Table 4.1. Barometric pressure at various altitudes.

Barometric pressure, B inches	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
	Feet	*Feet*	*Feet*	*Feet*	*Feet*	*Feet*	*Feet*	*Feet*	*Feet*	*Feet*
23.50	6,546	6,535	6,523	6,512	6,500	6,489	6,477	6,466	6,454	6,443
.60	6,431	6,420	6,408	6,397	6,385	6,374	6,362	6,351	6,339	6,328
.70	6,316	6,305	6,293	6,282	6,270	6,259	6,247	6,236	6,225	6,213
.80	6,202	6,190	6,179	6,167	6,156	6,145	6,133	6,122	6,110	6,099
.90	6,088	6,076	6,065	6,054	6,042	6,031	6,020	6,008	5,997	5,986
24.00	5,974	5,963	5,952	5,940	5,929	5,918	5,906	5,895	5,884	5,872
.10	5,861	5,850	5,839	5,827	5,816	5,805	5,794	5,782	5,771	5,760
.20	5,749	5,737	5,726	5,715	5,704	5,693	5,681	5,670	5,659	5,648
.30	5,637	5,625	5,614	5,603	5,593	5,581	5,570	5,558	5,547	5,536
.40	5,525	5,514	5,503	5,492	5,480	5,469	5,458	5,447	5,436	5,425
24.50	5,414	5,403	5,392	5,381	5,369	5,358	5,347	5,336	5,325	5,314
.60	5,303	5,292	5,281	5,270	5,259	5,248	5,237	5,226	5,215	5,204
.70	5,193	5,182	5,171	5,160	5,149	5,138	5,127	5,116	5,105	5,094
.80	5,083	5,072	5,061	5,050	5,039	5,028	5,017	5,006	4,995	4,985
.90	4,974	4,963	4,952	4,941	4,930	4,919	4,908	4,897	4,886	4,876
25.00	4,865	4,854	4,843	4,832	4,821	4,810	4,800	4,789	4,778	4,767
.10	4,756	4,745	4,735	4,724	4,713	4,702	4,691	4,681	4,070	4,659
.20	4,648	4,637	4,627	4,616	4,605	4,594	4,584	4,573	4,562	4,551
.30	4,540	4,530	4,519	4,508	4,498	4,487	4,476	4,465	4,455	4,444
.40	4,433	4,423	4,412	4,401	4,391	4,380	4,369	4,358	4,348	4,337
25.50	4,326	4,316	4,305	4,295	4,284	4,273	4,263	4,252	4,241	4,231
.60	4,220	4,209	4,199	4,188	4,178	4,167	4,156	4,146	4,135	4,125
.70	4,114	4,104	4,093	4,082	4,072	4,061	4,051	4,040	4,030	4,019
.80	4,009	3,998	3,988	3,977	3,966	3,956	3,945	3,935	3,924	3,914
.90	3,903	3,893	3,882	3,872	3,861	3,851	3,841	3,830	3,820	3,809
26.00	3,799	3,788	3,778	3,767	3,757	3,746	3,736	3,726	3,715	3,705
.10	3,694	3,684	3,674	3,663	3,653	3,642	3,632	3,622	3,611	3,601
.20	3,590	3,580	3,570	3,559	3,549	3,539	3,528	3,518	3,508	3,497
.30	3,487	3,477	3,466	3,456	3,446	3,435	3,425	3,415	3,404	3,394
.40	3,384	3,373	3,363	3,353	3,343	3,332	3,322	3,312	3,301	3,291
26.50	3,281	3,270	3,260	3,250	3,240	3,230	3,219	3,209	3,199	3,189
.60	3,179	3,168	3,158	3,148	3,138	3,128	3,117	3,107	3,097	3,087
.70	3,077	3,066	3,056	3,046	3,036	3,026	3,016	3,005	2,995	2,985
.80	2,975	2,965	2,955	2,945	2,934	2,924	2,914	2,904	2,894	2,884
.90	2,874	2,864	2,854	2,843	2,833	2,823	2,813	2,803	2,793	2,783
27.00	2,773	2,763	2,753	2,743	2,733	2,723	2,713	2,703	2,692	2,682
.10	2,672	2,662	2,652	2,642	2,632	2,622	2,612	2,602	2,592	2,582
.20	2,572	2,562	2,552	2,542	2,532	2,522	2,512	2,502	2,493	2,483
.30	2,473	2,463	2,453	2,443	2,433	2,423	2,413	2,403	2,393	2,383
.40	2,373	2,363	2,353	2,343	2,334	2,324	2,314	2,304	2,294	2,284
27.50	2,274	2,264	2,254	2,245	2,235	2,225	2,215	2,205	2,195	2,185
.60	2,176	2,166	2,156	2,146	2,136	2,126	2,116	2,107	2,097	2,087
.70	2,077	2,067	2,058	2,048	2,038	2,028	2,018	2,009	1,999	1,989
.80	1,980	1,970	1,960	1,950	1,940	1,930	1,921	1,911	1,901	1,891
.90	1,872	1,872	1,862	1,852	1,843	1,833	1,823	1,814	1,804	1,794
28.00	1,784	1,775	1,765	1,755	1,746	1,736	1,726	1,717	1,707	1,697
.10	1,688	1,678	1,668	1,659	1,649	1,639	1,630	1,620	1,610	1,601
.20	1,591	1,581	1,572	1,562	1,552	1,543	1,533	1,524	1,514	1,504
.30	1,495	1,485	1,476	1,466	1,456	1,447	1,437	1,428	1,418	1,408
.40	1,399	1,389	1,380	1,370	1,361	1,351	1,342	1,332	1,322	1,313
28.50	1,303	1,294	1,284	1,275	1,265	1,256	1,246	1,237	1,227	1,218
.60	1,208	1,199	1,189	1,180	1,170	1,161	1,151	1,142	1,132	1,123
.70	1,113	1,104	1,094	1,085	1,075	1,066	1,057	1,047	1,038	1,028
.80	1,019	1,009	1,000	990	981	972	962	953	943	934
.90	925	915	906	896	887	878	868	859	849	840
29.00	831	821	812	803	794	784	775	765	756	746
.10	737	728	718	709	700	690	681	672	663	653
.20	644	635	625	616	607	597	588	579	570	560
.30	551	542	532	523	514	505	495	486	477	468
.40	458	449	440	431	421	412	403	394	384	375
29.50	366	357	348	338	329	320	311	302	292	283
.60	274	265	256	247	237	228	219	210	201	192
.70	182	173	164	155	146	137	128	118	109	100
.80	91	+82	+73	+64	+55	+45	+36	+27	+18	+9
.90	0	-9	-18	-27	-36	-45	-55	-64	-73	-82
30.00	-91	-100	-109	-118	-127	-136	-145	-154	-163	-172
.10	-181	-190	-199	-208	-217	-226	-235	-244	-253	-262
.20	-271	-280	-289	-298	-307	-316	-325	-334	-343	-352
.30	-361	-370	-379	-388	-397	-406	-415	-424	-433	-442
.40	-451	-460	-469	-478	-486	-495	-504	-513	-522	-531
30.50	-540	-549	-558	-567	-576	-585	-593	-602	-611	-620
.60	-629	-638	-647	-656	-665	-673	-682	-691	-700	-709
.70	-718	-727	-735	-744	-753	-762	-771	-780	-788	-797
.80	-806	-815	-824	-833	-841	-850	-859	-868	-877	-885

ambient air. The source of the span gas may be a tank or other single-point SO_2 supply. The analyzer may have a programmable clock wired to solenoid valves so that zero and span operations occur at preset times without the need for operator assistance.

It is possible to set up a dynamic calibration system which will supply zero air and one or two span concentrations to the ambient air sampling line at preset intervals. At least one manufacturer (Metronics) offers such a system.

Suggested steps and explanations for performing zero and span operations are listed below.

1. Zero check. Manually or automatically switch the analyzer sample control (if the analyzer is so equipped) to the zero position. Mark the stripchart with time, date, and action. Enter the same information in the notebook. If the zero point is entered automatically in the operator's absence, be sure to note later the date, duration, etc., on the stripchart and in the station logbook. Be sure that the person ultimately responsible for data reduction and analysis is made aware of these operations so that such time intervals are accounted for. If an automatic data acquisition system is used, be sure that it does not treat the zero and span readings as ambient data.

   Allow sufficient time for a stable zero signal to occur. If the system is automated, program the clock for ample time. If the zero air source requires warmup, allow time for this, too. Make no adjustments to the analyzer at this time.

> NOTE. The system used for the multipoint calibration may also serve as a zero and span source. First, be certain the system is warmed up and flows are calibrated. Then connect the analyzer to the calibration manifold in the same way as in a multipoint calibration.
>
> Such a zero and span operation is often performed just prior to a multipoint calibration. In this way, changes in analyzer response since the last

multipoint calibration are determined by an accurate, reliable, dynamic calibration source.

2. Span check(s). Set up the span gas supply so that an accurately known concentration of approximately 80 percent of full scale is generated. Turn on the single-point span gas supply by manual or automatic means. Mark the stripchart and enter time, date, and action in the notebook.

Follow all the manufacturer's instructions for installation and use of the span gas source. Allow sufficient time for the span gas supply to equilibrate and for the response of the analyzer to stabilize. With automated systems, program the clock for ample time. Make no adjustments to the analyzer.

NOTE. The system used for the multipoint calibration may also serve as a span check source. If possible, the same span concentration as used during the last multipoint calibration should be generated so a direct comparison can be made. If this cannot be done, the concentration that is generated should be compared to the expected value (or voltage) based on the calibration curve or calibration equation established for the most recent prior calibration. This comparison could be made by: (1) solving the least squares regression equation for the expected response (mv, volts, or chart divisions) to the known SO_2 span concentration you are generating, or (2) finding the expected response on a carefully drawn calibration graph of the analyzer response versus SO_2 concentration.

3. Disconnect the zero and span system. Be certain that the analyzer ceases to sample zero or span gas and is returned to ambient air. When the span check ends, allow sufficient time for the analyzer response to "recover" from the span signal. This will be evident from the stripchart trace. The time at which recovery is complete should be recorded as the "end time" for zero and span operation. This will also be the time at which valid ambient air data are

again recorded. Denoting this time is particularly important when an automatic data acquisition system is used.

4. Correct problems indicated by zero, span data. As a general rule, no adjustments are made to the zero and span settings of an analyzer during a zero and span check. This is because of several reasons. The zero or span source is often not as accurate as the dynamic calibration system. Minor variations (noise) in instrument zero and span response are expected and cannot be adjusted out. Large changes in atmospheric pressure or CO_2 levels of cleaned ambient air can affect the span signal somewhat and daily adjustment cannot compensate for this.

   If gross variations (greater than 5 percent, the percent allowable drift for an EPA equivalent-designated instrument) are noted in either the zero or span check, or if the zero or span is slowly but steadily changing in one direction over a period of days, action should be taken. First, check the zero and span sources for reliability by comparison to calibration standards or by performing a dynamic calibration. If they are correct, the analyzer itself needs corrective maintenance and a multipoint calibration.

4.4 MAINTENANCE AND REPLACEMENT OPERATIONS

Following the zero and span check and just prior to a multipoint dynamic calibration, maintenance and replacement activities are carried out. Any maintenance on the station itself (such as air conditioning adjustment or cleaning of ambient air intake) is also done at this time. A record of all items replaced or adjustments made should be entered in an appropriate notebook or logbook. A supply of replacement gases, filters, and parts should be maintained at the central laboratory.

It is suggested that the following minor maintenance and replacement steps be performed prior to each monthly multipoint calibration. Special conditions such as dusty environments may necessitate more frequent maintenance.

1. Check gas supplies. Replace empty or near-empty gas cylinders of hydrogen, air, or others. Service H_2 generators by adding water

or electrolyte. Refer to the manufacturer's instruction manual. If the FPD analyzer flames-out when the H_2 supply is replaced, relight the flame as soon as possible to avoid long restabilization times.

Check all connections between the H_2 supply and the analyzer to be certain they are leaktight. Use a liquid leak detector.

2. Replace filters; clean or replace sampling lines. Often a Teflon membrane filter and Teflon filter holder are located in the ambient air sampling line leading to the analyzer. Some operators make a practice of replacing this filter prior to each multipoint dynamic calibration. Do not allow too much particulate matter to build up on the filter before replacing it. Replace the filter and clean the holder prior to calibration. Figure 4.1 shows a typical filter and holder and gives directions for its assembly.

> CAUTION. Be sure the Teflon filter is seated properly and the filter holder is reassembled tightly. If not, a leak will exist and particles may reach the FPD burner. Exercise care not to overtighten Teflon threaded connections. If the thread are stripped, a poor seal results.

Another filter which may need to be replaced is located at the rear of the analyzer at the dilution air entry. Replace it with an identical filter. Some analyzers have a coarse sintered brass filter located on the pump inside the case. The sintered filter should be replaced after about 1 year of continuous operation.

> CAUTION. The dilution air filter holder is often attached to a hypodermic needle which pierces a rubber septum and acts as a critical orifice. This supplies a constant flow of dilution air to dilute the moist burner exhaust air and prevent unwanted water condensation.
>
> If the needle must be removed to replace the filter holder, be sure it is put back exactly as it was. Be careful not to obstruct the needle by clogging it with a piece of rubber septum material. If the

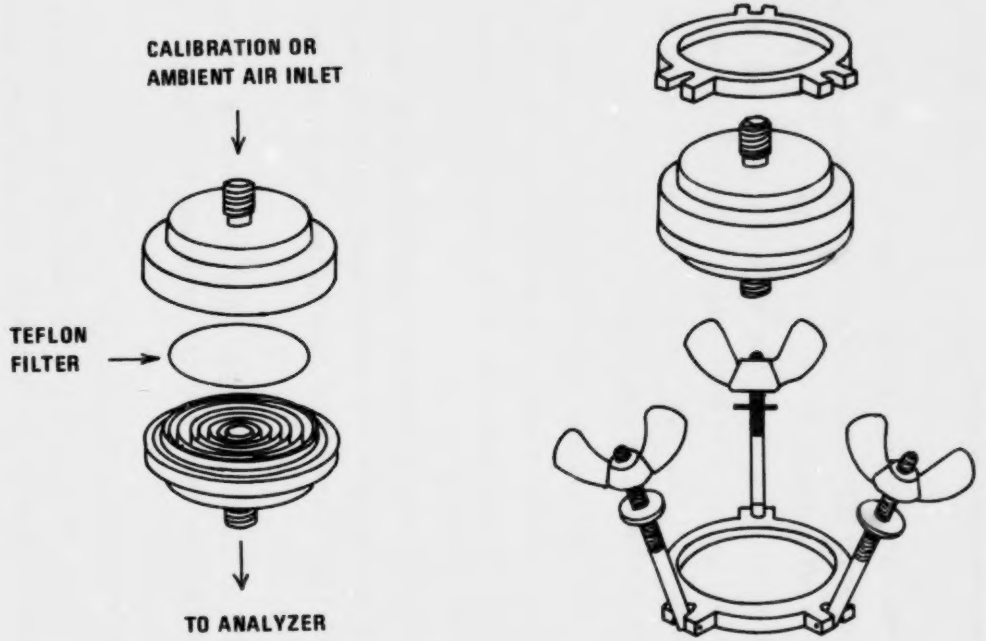

CALIBRATION OR
AMBIENT AIR INLET
TEFLON
FILTER
TO ANALYZER

Figure 4.1. Sampling line filter holder and filter of all-Teflon construction.

needle is replaced, the new one should be of exactly the same length and gauge as the old one in order to avoid large flow changes. If the rubber septum is cracked or not seated properly, replace it too.

CAUTION. If the dilution air filter is replaced with one quite different from the original, flow changes in both the dilution air and the sample air may occur. Calibration errors, flameout, and other problems may also occur.

The ambient air sample line itself, 3.2 mm (1/8 in) o.d. Teflon, may occasionally need replacement because of a buildup of particles or occurrence of "kinks" in the line. If so, cut and install a new piece of exactly the same length as the one it replaces. Use only Teflon fittings; check all fittings for tightness. Any new tube or filter will require a conditioning period with SO_2 before a stable, steady signal is attained.

The lines may also be cleaned by removing them, flushing with pure methanol (methyl alcohol, a poison), and venting zero air or dry nitrogen through the tube until it is dry. Recondition the lines with SO_2 calibration gas.

3. Leak check. Any pneumatic connections that were untightened during maintenance and replacement should be leak-checked. Use a liquid leak detector or pure water. Wipe off the fluid after testing.
4. Perform other maintenance. Any maintenance or repair of the stripchart recorder and the data acquisition system should be done at this time.
5. Adjust instrument flow rates.
    a. Carefully adjust the hydrogen flow rate control knob. Hydrogen flow will be indicated by a pressure gauge or rotameter or both. Set the gauge or rotameter to the position specified in the operating manual. Record both the old and new settings in notebook.

b. Carefully adjust the air sample flow rate control knob. Some analyzers, such as the Meloy Model 285 and the Monitor Labs Model 8450 have preset sample flow rates which cannot be adjusted. Sample flow will be indicated by a rotameter, but usually only when the analyzer is in the zero mode. Set the rotameter to the manufacturer's suggested setting. Determine the actual ambient mode flow rate by attaching the analyzer sampling line to the upper part of a soap film flowmeter. Refer to Section 5 for explanation of use. Record the flow value in the notebook.

Any major maintenance on the FPD analyzer should be done prior to calibration. Be sure to allow enough time for the analyzer to warm up again before beginning calibration. Consult the manufacturer's instruction manual for details of major maintenance operations. Major maintenance items include:

1. Sample pump overhaul or replacement,
2. Photomultiplier tube replacement,
3. Solenoid valve replacement,
4. H_2S scrubber replacement or reconditioning,
5. Cleaning or replacement of rotameters or gauges,
6. Cleaning of the burner block, and
7. Cleaning or replacement of the cooling fans.

4.5 MULTIPOINT CALIBRATION OF AN FPD SO_2 ANALYZER EQUIPPED WITH A LINEARIZED OUTPUT

A multipoint calibration must be performed when the analyzer is first set up and periodically thereafter. The frequency of calibration will depend upon the type of sample the analyzer receives, the environmental conditions under which the analyzer operates, and the requirements for data accuracy. Only by performing frequent calibrations (at least monthly) can the reliability and accuracy of air quality data be maintained and assessed. Dramatic changes in calibration results alert the user to problems with the analyzer or calibrator. Periodic calibrations are an important part of the quality control and quality assurance aspects of an air monitoring program.

The following procedure is intended for use with instruments that are designed to sample the ambient atmosphere for SO_2. Under these conditions, the SO_2 level often will be low (often 0.1 ppm or less) and measurements of the highest accuracy are sought. To help insure the accuracy of the data, the analyzer should be operated under controlled environmental conditions of temperature, voltage, and humidity, and the calibration procedure should be performed frequently.

A multipoint calibration should be performed soon after receipt of a new analyzer and monthly thereafter. In addition, a multipoint calibration should be carried out:

1. Following any adjustments or replacements of amplifier assemblies, power supply boards, temperature control boards, or photomultiplier tube;
2. If for any reason the air sample flow rate or hydrogen flow rate is adjusted from previously set or recommended values (these flows affect the flame and, thus, affect the response); and
3. If the burner assembly or any Teflon lines are cleaned or replaced.

A dynamic calibration should always be performed at the site of the analyzer. Do not calibrate an instrument at one location, move it to another, and expect the calibration to "hold."

Step-by-step instructions for dynamic calibration of a typical FPD SO_2 analyzer (using the linearized output) are given below. Each step is numbered. Special explanations or precautions are given immediately following the instructions. Figure 4.2 is a reproduction of the stripchart trace of a typical multipoint calibration and should be consulted as one proceeds with the calibration.

1. Verify that PRELIMINARY STEPS, ZERO AND SPAN CHECK, AND MAINTENANCE AND REPLACEMENT steps are complete. Record all actions and results in a notebook or the calibration logbook.
2. Interface the analyzer and the calibration system. Disconnect the analyzer's Teflon ambient air sampling line from the station ambient air sampling manifold and connect it to the calibration system manifold.

> The ambient air sampling line should be used for calibration purposes. In this way the calibration

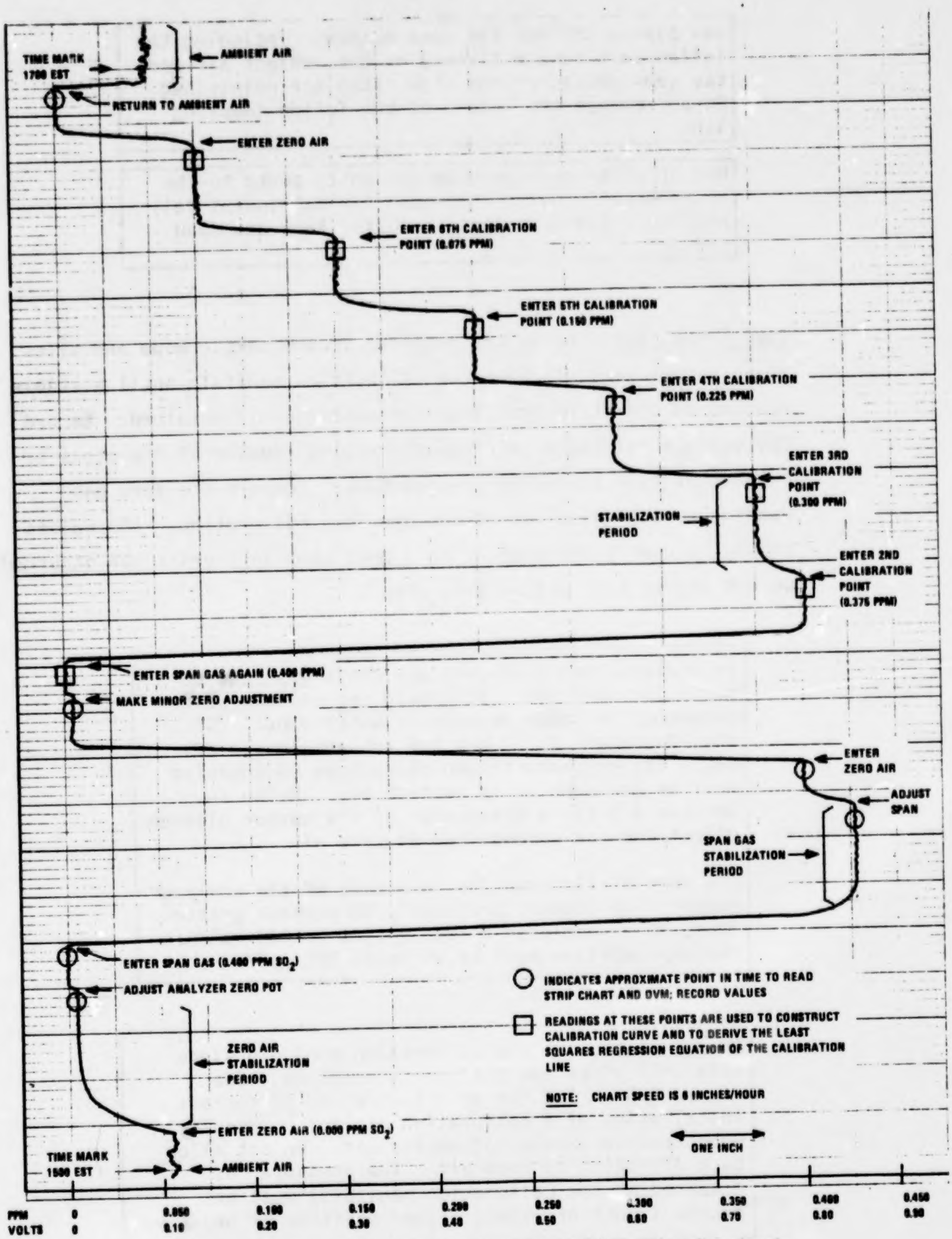


Figure 4.2. Calibration trace of linearized output. FPD ambient air SO_2 analyzer.

gas passes through the same pathway (including the Teflon particulate filter) as the ambient air and the same pressures and flow rates are maintained. Do not change the length of the Teflon sampling line.

Use of other zero or span gas entry ports to the instrument is not recommended for multipoint calibration. Use such ports only for zero and span checks.

3. Sample zero air. Leave the analyzer in the sample mode and allow it to sample zero air from the calibration manifold until a stable reading on the stripchart trace or voltmeter is obtained. Record the voltage reading or stripchart reading (number of divisions or percent of full scale) in the notebook. Compare the zero gas reading to the value set at the previous calibration. The values should be nearly the same if no significant zero drift has occurred. Do not adjust zero pot at this time.

Be certain that your zero air meets all requirements for zero air. It should not contain sulfur compounds or large amounts of water vapor. It should contain ≅ 350 ppm (or ambient levels of) CO_2. The oxygen/nitrogen percentage composition must be the same as in ambient air. Refer to Section 3.0 for a discussion of the carbon dioxide effect and the composition of zero air.

The zero airflow must be in excess of the analyzer sample flow demand, preferably 50 percent greater. Thus, if an analyzer's sample flow is 200 cm^3/min, the zero airflow must be at least 300 cm^3/min.

Do not pressurize the calibration manifold since this will alter the analyzer's response. See Figure 3.6 or 3.7 for an illustration of correct installation of a calibration manifold. Provide unobstructed exhaust of excess air. Do not allow back diffusion of room air. The pressure (as measured at the calibration manifold) must not exceed 1 inch of water, either positive or negative, from the ambient pressure. Use a water manometer for measuring pressure. Refer to Section 5.0 for instructions on its use.

As long as 30 minutes or more may be required to obtain a stable zero baseline. This is usually the case when a high SO_2 concentration has been sampled just prior to sampling zero air. The analyzer should have been on for at least 24 hours prior to calibration.

4. Set the zero of the analyzer. Set the front panel zero adjust pot so that the analyzer output, as measured by the digital voltmeter, DVM, reads 0.000 V or the value given by the manufacturer for the linearized output. (For example: 0.000 V for Monitor Labs Model 8450; 0.014 volts for Meloy Labs Model SA-185-2A.) Do not set zero by adjusting the recorder zero.

PRECAUTION! If your FPD SO_2 analyzer is a model 8300 manufactured by the Bendix Corporation, do not adjust the front panel zero adjust. Internal adjustments of the nonsulfur suppression pot may be required. Refer to the Bendix operation manual for assistance or see Section 4.6.1 for procedures and explanations. Calibration of Bendix FPD analyzers continues with Step 5.

If your analyzer is manufactured by Meloy Laboratories and you wish to use the log output instead of the linearized output, refer to Section 4.6.2 for further details. Instructions for offsetting zero of Meloy instruments are given in Section 4.6.3.

The pen of the stripchart recorder should trace a line at the point on the chart paper corresponding to 0.000 V (or the voltage value assigned to zero ppm SO_2). Stripchart divisions, percent of full scale chart readings, or ppm SO_2 values taken from the recorder may be used instead of voltmeter readings. Be certain the recorder itself is properly zeroed, spanned, and its response is linear. See Figure 4.2 for an example of voltage and ppm SO_2 readings assigned to a stripchart.

Allow a few minutes following zero pot adjustment to be sure a stable voltage is obtained, then "lock" the zero pot and record the voltage value in notebook.

Sometimes the process of "locking" the zero pot causes a slight change in the setting. Be aware of this and make necessary adjustments.

If an unusually large adjustment is necessary, or if the zero point cannot be set by adjustment of the pot:

a. Be sure the analyzer has been given sufficient time to stabilize on zero air (check strip chart for no further change in slope of the trace).

b. Be sure there is no source of SO_2 or other sulfur compound entering the zero air.

c. Be sure the charcoal scrubber for the zero air supply is fresh.

d. Be sure the flame is lighted.

e. Consult manual or manufacturer for troubleshooting and servicing procedures.

5. Sample SO_2 span gas. Adjust the flow rate of the calibration assembly to produce an SO_2 span gas of concentration equal to approximately 80 percent of the value of the analyzer's range. The usual ranges used are 0 to 0.5 or 0 to 1.0 ppm. If, for example, the analyzer is set to a 0-0.5 ppm range, 80 percent of the range would be (0.80) (0.5) = 0.4 ppm. Generate this concentration (0.400 ppm) or an accurately known value close to it. Use

this as the span gas concentration. Instructions are given in Section 3.0. Sample the span gas until a stable signal is obtained (as indicated by the stripchart trace). Record the voltage value or stripchart reading in the notebook as "unadjusted span" value.

A permeation tube type calibrator, whose tube is traceable to NBS standards, is recommended for generating all SO_2 concentrations for span and intermediate concentrations. Be certain the diluent air (carrier air) is of the same composition as the zero air. See Section 3.0 for details of the use of such calibration devices, calculation of the SO_2 concentration, and the use of SO_2 from cylinders as calibration gases.

Provide a flow of span gas that is at least 50 percent in excess of the analyzer's flow requirement.

As long as 30 minutes may be required for signal stabilization, especially if the analyzer is new or if new tubing or a new H_2S scrubber has been installed, stabilization may take several hours. This is due to the "conditioning" of "active sites" in the Teflon line and scrubber by SO_2. Usually 10-15 minutes should suffice for stabilization.

If the analyzer response goes "offscale" and does not soon return, remove the sampling line from the manifold momentarily and check to see if the analyzer and recorder are on the correct range. Also, check the dilution air flow setting of the calibrator.

Another cause of offscale readings is excess SO_2 from a permeation tube that has remained in its compartment without air passing over it continuously. If this is the case, the calibrator must be flushed with clean air for some hours before the calculated concentration is obtained.

6. Compare "unadjusted span" value to previous calibration results. Using the previous calibration curve or equation and the "unad-

justed span" reading determined in Step 5, determine the concentration of SO_2 being indicated by the analyzer. Compare this result to the calculated span gas concentration being used in Step 5. The calculated concentration is based on the permeation device output and measured dilution airflow rates. Compute the percent difference between the two values.

Example calculation. Based on the previous multipoint calibration curve, the indicated SO_2 span concentration is measured as 0.392 ppm. The concentration based on the permeation tube weight loss and known dilution flow rates, is 0.430 ppm.

Thus:

$$\frac{\textbf{Indicated Concentration} - \textbf{Calculated Concentration}}{\textbf{Calculated Concentration}} \times 100 = \textbf{percent deviation}$$

$$\frac{0.392 - 0.430}{0.430} \times 100 = -8.84 \text{ percent}$$

If the values are within ±10 percent, proceed to Step 7.

If the present span concentration is greater than ±10 percent of the value predicted by the previous calibration data, a problem may exist in the present calibration setup, a problem was present at the last calibration, or the analyzer has drifted significantly and needs maintenance. Check the present calibration using the following steps.

Check the calibration system for:

a. Proper dilution airflow setting (redetermine actual airflow if necessary and recalculate SO_2 concentration if an error was made).

b. Sufficient airflow to the analyzer. (50 percent excess flow is desirable.)

c. Proper temperature and temperature control of permeation oven.

d. Line voltage variations.

e. Leaks.

f. Permeation tube integrity.

g. Proper CO_2 content of diluent air.

Check the FPD Analyzer for:

a. Correct and stable sample flow rate.

b. Correct H_2 flow rate.

c. Obstruction-free exhaust.

Check the recorder for correct span.

> If no fault is found in any of these checks, the analyzer may need electronic adjustment. Refer to the manufacturer's manual or consult the manufacturer. It is also possible that the previous calibration was in error; it should be reviewed for errors.

7. Set the analyzer span. Calculate the expected analyzer voltage output and/or recorder response (chart divisions or percent of full scale) for the calculated concentration of span gas. Adjust the front panel span pot so that the linearized output reads the correct value on the DVM and/or the stripchart.

> Example computation. If the analyzer is set on the 0-0.5 ppm range and has a 0-1 V linearized output, and the calibration system is set to give 0.400 ppm SO_2, the predicted voltage is computed as follows:
>
> $$\frac{\text{calibrator span, ppm}}{\text{analyzer range, ppm}} \times \text{analyzer full scale voltage output} = \text{voltage span point}$$
>
> $$\frac{0.400 \text{ ppm}}{0.500 \text{ ppm}} \times 1 \text{ volt} = 0.800 \text{ V}$$
>
> The recorder should trace a steady line at an upscale point. If the recorder is on the 0-1 V range, the stripchart has 100 chart divisions, and the recorder zero is set at 5 percent of full scale (i.e., five chart divisions), then 0.400 ppm SO_2 should give a trace at:

$$\frac{0.400 \text{ ppm}}{0.500 \text{ ppm}} \times (100 \text{ divisions}) + (5 \text{ divisions}) =$$

80.0 + 5 = 85.0 chart divisions

Refer to Figure 4.2 for illustration.

8. If the span adjustment required in Step 7 was appreciable (±5 percent of the expected value), return the analyzer to zero air (Step 3), allow the analyzer to stabilize, and make necessary adjustments of the zero pot.
9. Return to the span gas, allow the analyzer response to stabilize, and make necessary adjustments of the span pot.
10. Repeat zero and span gas operations until it is no longer necessary to adjust the zero or span pots.
11. Adjust the calibrator flow rates to generate in succession the following standard SO_2 calibration levels (expressed as percent of instrument range):

approximate percent of range	ppm, if 0.5 ppm range
75	0.375
60	0.300
45	0.225
30	0.150
15	0.075

Other levels may be introduced if desired. Values less than 0.100 ppm are suggested since ambient SO_2 concentrations are usually in this range. Values less than 0.040 ppm (40 ppb) are very slow to give a stable response.

Important! Make no adjustments to the zero or span pots while these points are being entered.

Record the voltage or stripchart response for each level.

Introduction of an SO_2 concentration equal to exactly 75 percent, 60 percent, etc. of full scale range is not necessary. What is important and necessary is that these concentrations be equally spaced over the range; be within ±5 percent of the 75 percent, 60 percent, etc., level; and that the concentration be prepared with accuracy (within 0.001 ppm).

Allow sufficient time for each SO_2 level to stabilize ("level off" as indicated by the stripchart) before proceeding to the next value.

The instrument response time and stabilization time will be slower at the lower concentration values.

12. Construct a plot of the calibration data on graph paper. Refer to Figure 4.3 as an example.
    a. Use a high quality graph paper with fine graduation marks so that data points may be clearly entered. A good choice is 18 x 25 cm graph paper with 10 x 10 divisions to the centimeter.
    b. Assign the SO_2 concentration values to the x-axis (horizontal axis). These are the calculated values from the calibration system. Subdivide the x-axis in ppm extending from zero to the analyzer's full scale range. Units of micrograms of SO_2 per cubic meter ($\mu g/m^3$) may also be plotted; 1 ppm SO_2 = 2,615 $\mu g/m^3$ SO_2 at 1 atmosphere (760 mm Hg) and 25° C. Assign the analyzer response (V or mV or percent of scale) to the y-axis (vertical axis) and subdivide this axis into portions of the full scale output for the particular analyzer (0-1 V, 0-100 mV, etc.).
    c. Enter the zero and span values on the graph, also enter all intermediate calibration values.
    d. Check the quality of the calibration curve in the following way:

       With the aid of a straightedge (ruler, etc.) connect the zero and span points with a light pencil line.

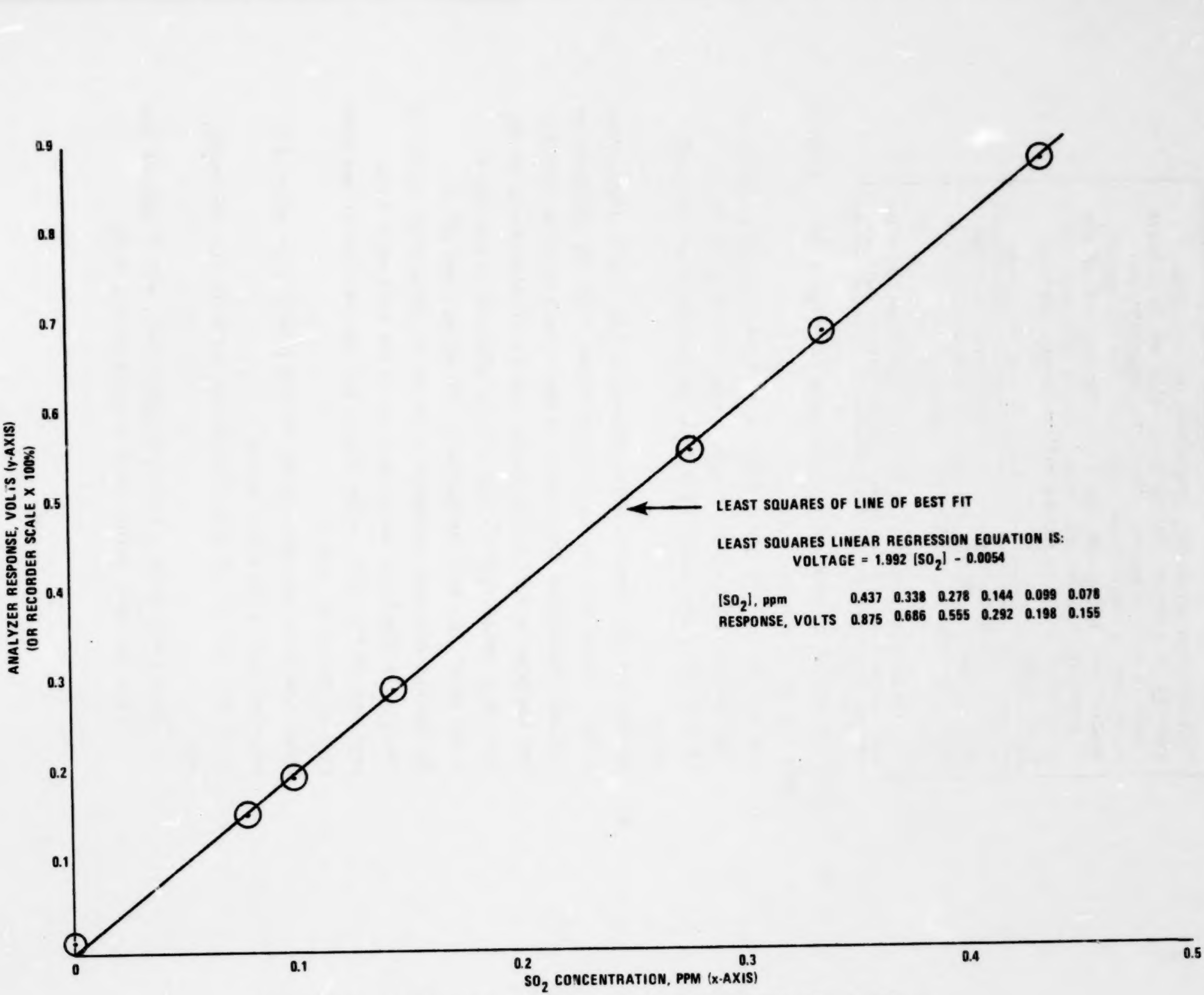


Figure 4.3. Calibration curve for linearized FPD SO$_2$ analyzer.

Look at the positions of the intermediate calibration points with respect to the straight line. The intermediate points should fall on or very near the line. If they are all off, either above or below the line, this may suggest:

The span point is incorrectly set. Recheck the air flow and calculations used for spans.

The zero point is incorrectly set.

The linearization circuitry of the FPD analyzer is in need of adjustment. Refer to operation manual or to manufacturer for aid. All possible error sources should be investigated before adjustments are made to the linearization circuitry. Unless you are thoroughly familiar with this circuitry, it is best to consult the manufacturer for advice.

13. Determine the calibration equation. Determine, or have determined by someone, the equation for the least squares line of best fit for all the calibration points, including zero and span.

> Many hand-held calculators now have the capacity to compute the least squares linear regression equation.

The equation will be of the form $y = mx + b$ where:

y = analyzer response (V),
m = slope of calibration line (V per ppm),
x = concentration of SO_2 (ppm), and
b = intercept of the calibration line with the y-axis (V).

Using this equation, calculate the location of any two points on the line (one point near zero, one point near full scale). Connect these points with a light line and extend the line through the y-axis as well as beyond the span point. This line should pass through or very near to the intermediate calibration points, the span point, and the zero point. Refer to Figure 4.3.

Apply the equation to convert voltage signals stored on a data acquisition system to concentration units. Forward the calibration record and the least squares regression equation (if computed) to your supervisor or to the data processing department. This equation will be used to treat the signals stored in a DAS until the time of the next calibration.

The equation may also be used to solve for ppm SO_2 concentrations corresponding to voltage values taken manually from the stripchart. If the calibration points lie on or very close to the calibration curve, the SO_2 values may be read directly from the stripchart.

Example calculations:

x-axis SO_2, ppm, from permeation tube calibration		y-axis Linear response, volts (0-1 V output; analyzer range 0-0.5 ppm)	
0.0	zero air	+0.0136	(set with zero pot)
0.437	span gas	0.875	(set with span pot)
0.338		0.686	
0.278		0.555	
0.144		0.292	
0.099		0.198	
0.078		0.155	

Least squares linear regression equation is:

$$\text{voltage} = 1.9921\ [SO_2] + 0.0054$$

or, rearranging:

$$[SO_2]_{ppm} = \frac{\text{voltage} - 0.0054}{1.9921}$$

Thus, for example, if a known concentration of SO_2 of 0.500 ppm is sampled by the analyzer, the expected response is:

$$\text{voltage} = 1.9921\ (0.500\ \text{ppm}) + 0.0054$$
$$\text{voltage} = 1.001$$

As another example, if a voltage value of 0.300 is obtained, the equation says that the concentration of SO_2 is:

$$[SO_2]_{ppm} = \frac{0.300 - 0.0054}{1.9921} = 0.148 \text{ ppm}$$

14. Return the analyzer sampling line to the station sampling manifold and ambient air. Make note of this action and the time in the notebook.

4.6 SUPPLEMENTARY INSTRUCTIONS FOR PARTICULAR FPD ANALYZERS

4.6.1 Bendix Model 8300: Electronic Zero and Operational Zero

The Bendix Model 8300 FPD SO_2 analyzers have two adjustable zero pots which serve different purposes. One is located on the front panel; it is an electronic zero and is adjusted only when the flame of the FPD is extinguished. The second zero, located inside the cabinet, is often called the nonsulfur suppression adjustment, and is adjusted only when the flame is burning and zero air is being sampled. If your instrument is a new model (not Model 8300) the following instructions do not apply. For instance, the Model 8303 would not use these instructions.

4.6.1.1 Front panel electronic zero adjustment

Adjustment of the front panel electronic zero must be made while the flame is extinguished. The following steps are taken from the Bendix operation manual.

1. Extinguish the flame by pulling the PULL TO TEST hydrogen diverter valve fully out. Be cautious when venting hydrogen. A tube should be attached to the vent to carry the hydrogen to the outside air.
2. When the flame is out, if a positive output is indicated by the voltmeter or recorder, adjust the ZERO adjustment pot on the front panel of the analyzer for a zero indication on the voltmeter or recorder. This adjustment corrects for the offset of the amplifiers in the Exponential Amplifier Card.

> NOTE: Usually the ten-turn ZERO adjustment pot indicator dial is factory-set at midscale; ~500, and will give a 0.001 V output when the 0-1 V range output (located on the rear panel) is connected to

a digital voltmeter. If the voltmeter or recorder indicates that adjustment is necessary, the ZERO pot should require adjustment by only a few divisions.

3. If a 5 percent offset of full scale and zero of the analyzer is desired, use the front panel ZERO adjustment pot at this time. For example, if the analyzer is in the 0-1 ppm range and has a 0-1 voltage output, the pot should be adjusted until the voltmeter or recorder indicates 0.050 V (50 mV). This gives a "live zero." See comments in Section 4.6.3 describing the effects of this zero offset on the data.
4. After electronic zero adjustment is complete, return the hydrogen diverter valve to the "in" position and relight the flame.

4.6.1.2 Internal operational zero (Nonsulfur Suppression) adjustment

1. The instrument should be on, the flame should be lighted, and the instrument should be sampling zero air.
2. Carefully remove the top cover of the analyzer and adjust the NONSULFUR SUPPRESSION pot (located on an interior panel of the instrument) until a zero voltage is indicated on the voltmeter or recorder. This adjustment is very critical. Extreme misadjustment can cause a negative voltage readout. Misadjustment also tends to cause nonlinear response, especially at low levels.

> WARNING. The NONSULFUR SUPPRESSION pot is the biasing pot for the photomultiplier tube log amplifier. If it is turned too far negative, it will bias the amplifier in an OFF position and a certain concentration of SO_2 will be required to turn the amplifier on. This, in effect, causes loss of detection of low-level sulfur concentrations.
>
> If the pot adjustment is too positive it will cause the amplifier to come on and show a positive response in the absence of of SO_2. In this condition, nonlinear behavior is also observed.

3. Operate the instrument on zero air for 30 minutes to be sure there is no zero drift.

4. Return to the calibration procedure, Section 4.5 of this document, and continue with the span adjustment.

4.6.2 Use of the Optional Log-Linear Output of Meloy FPD Analyzers

There are several signal outputs available from various models of the Meloy (or the earlier Melpar) FPD SO_2 analyzer. These are the log-log output (plotted as log of amperage versus log of concentration), and the linearized output (plotted as linear voltage versus linear concentration).

The linearized output is most commonly used and most instruments are purchased with the optional linearization circuit included. Linearizing circuitry "packages" are also available. A discussion of the log-log and log-linear outputs is given below.

4.6.2.1 Log-log output

The output signal from the photomultiplier tube is in the form of an electrical current. This signal is an exponential function which plots linearly versus concentration on log-log paper with a slope of 1.4 to 2.0, depending on the burner characteristics. Figure 4.4 shows a log-log plot of SO_2 concentration, ppm, versus the photomultiplier current output of a typical Meloy FPD SO_2 analyzer.

The log-log output is not commonly available on Meloy ambient air analyzers. The output more commonly available at the rear panel is the log-linear output discussed below.

4.6.2.2 Log-linear output

Meloy Laboratories employs a patented amplifier which converts the current from the PM tube to a voltage. This amplifier also has a log response which is adjustable so that a 0-1 V output may represent up to six decades of input current. By using this log/linear amplifier, a wide dynamic range is obtained with excellent readability for low SO_2 concentrations.

Figure 4.5 is a plot of typical calibration data, and shows SO_2 concentration, ppm, versus the voltage output from the log/linear amplifier. In this particular instrument, a voltage output of 0.000 V corresponds to 0.000 ppm SO_2 and 1.000 V to 0.500 ppm SO_2. Note that the output is plotted on semilog graph. The SO_2 concentration is plotted on the logarithmic x-axis, the analysis response, volts, is entered using the linear y-axis.

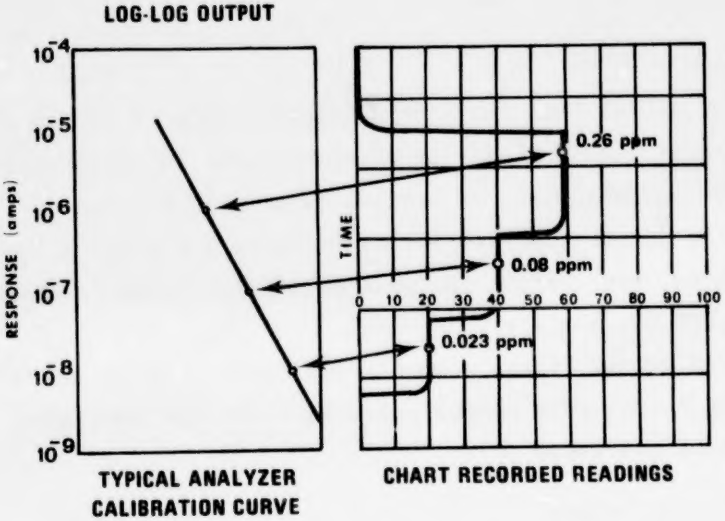


Figure 4.4. Log-log output of the Meloy Model SA 185 FPD SO_2 analyzer.

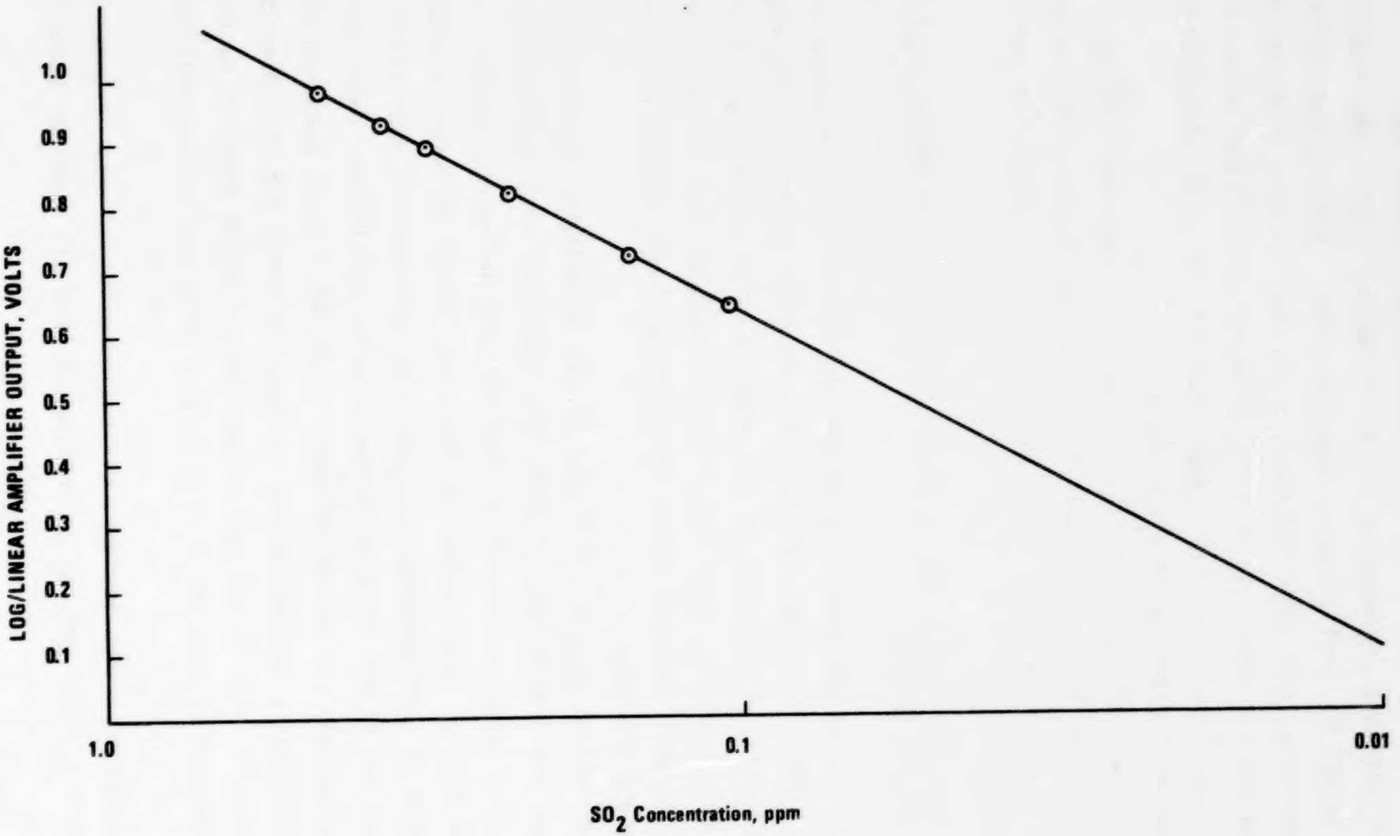


Figure 4.5. Log-linear plot of calibration data, Meloy model SA 185-2A FPD SO_2 analyzer.

Other concentrations of SO_2 may be read from the curve if the voltage output of the calibrated analyzer is known. For example, a voltage output of 0.460 corresponds to an SO_2 concentration of 0.048 ppm.

If data are recorded on linear stripchart paper, the concentration value cannot be read directly from the chart. Instead the voltage value (or alternatively, the number of chart divisions) is read from the stripchart and the ppm (or $\mu g/m^3$) value taken from the calibration curve (e.g., Figure 4.5). Logarithmic stripchart paper may also be used. Concentration values are then read directly from the chart.

If log/linear voltage data are stored on magnetic tape by a data acquisition system, an equation must be employed to convert the raw voltage signal to physical units. Such an equation is developed in Section 4.6.3 of this document.

4.6.3 Data Correction Due to Baseline Offset of the Meloy Lab's Model SA 185 Output

Some users may prefer to offset the "zero" baseline output of Meloy Model SA 185 FPD sulfur analyzers to some point higher on the output voltage scale to allow observation of any negative drift which might occur. Indeed, in the early models, which use electronic rather than thermal flame-off detection, such negative drift can cause hydrogen shutoff with subsequent unnecessary downtime.

When offset is used, the data of the normalized logarithmic output are no longer applicable and an error, the magnitude of which depends on the amount of offset, is introduced into the data being collected.

The maximum error occurs at the lower levels of concentration due to the nature of the logarithmic curve. The mathematical expression used to calculate the effect is given below. Correction tables, calculated from that expression, for offset voltages of +0.065 V (0.01 ppm) and +0.147 V (0.015 ppm) for a typical SA 185 calibration curve are also provided. In the data shown with a 0.01 ppm offset the precision error is no greater than +0.003 ppm and is reduced, in the area of 0.04 ppm, to insignificance (±0.001 ppm).

Two possibilities for data correction exist. First, a gross error of approximately 0.003 ppm can be subtracted from all readings below 0.040 ppm.

Second, an exact correction based on an equation and the calibration curve supplied with your unit(s) can be used either manually or with a computer, if that type of data treatment is desired. A computer can be programmed easily to correct each data point or to provide a correction table.

There is a third possibility. It is to accept the readings without correction, knowing that a possible error of +0.004 ppm at very low concentrations exists but is not significant enough to cause concern.

The equation used to determine actual concentration versus output signal when the baseline (zero gas value) is offset (that is, the output zero value is greater than zero) is:

$$[SO_2] = 0.007260\ [e^{V_R A} - e^{V_0 A}]^B$$

where:

$[SO_2]$ = actual concentration, ppm

e = natural logarithm base = 2.71828

V_R = output signal voltage with sample divided by output voltage at 1 ppm (Full Scale)

V_0 = output voltage with zero gas introduced to analyzer divided by output voltage at 1 ppm (Full Scale)

$A = 1.0695\ [\ln (A_1/A_0)]$

$B = \dfrac{(4.6052)}{[\ln (A_1/A_0)]}$

A_1 = current output in amps from calibration curve at 1 ppm SO_2

A_0 = current output in amps from calibration curve at 0.010 ppm SO_2

ln = natural log of value in parenthesis

An example of the equation use and the resulting error using a typical calibration curve is:

$A_0 = 4.55 \times 10^{-9}$ amps at 0.01 ppm SO_2

and

$A_1 = 3.85 \times 10^{-5}$ amps at 1.0 ppm SO_2

therefore:

$$\ln(A_1/A_0) = 9.0433$$

$$A = 1.0695\ (9.0433) = 9.672$$

$$B = \frac{(4.6052)}{(9.0433)} = 0.5092$$

with a baseline offset of 0.065 V (0.01 ppm on the meter):

$$e^{V_0 A} = e^{(0.065)\ (0.672)} = 1.875$$

using this "typical calibration curve" data for Table 4.2 were prepared. As can be seen from Table 4.2, the error is only 0.003 ppm when the meter or output reads 0.020. The error quickly decreases so that at a reading of 0.05 ppm or greater there is essentially no error due to the offset (a %0.001 ppm variation is attributed to mathematical error due to rounding off).

Table 4.3 shows the effect of a 0.015 ppm offset. The error, although greater at very low concentrations, becomes insignificant at 0.07 ppm concentration level.

Table 4.2. Typical effect of an offset of 0.065 V (0.01 ppm)

V_R	Meter Reading SO_2 (ppm)	Actual Concentration (ppm)	Error (ppm)
0.065	0.01	0.000	Not Applicable
0.206	0.02	0.017	+0.003
0.288	0.03	0.028	+0.002
0.346	0.04	0.039	+0.001
0.392	0.05	0.049	+0.001
0.533	0.10	0.100	0
0.673	0.20	0.199	+0.001
0.756	0.30	0.300	0
0.859	0.50	0.499	+0.001
0.928	0.70	0.701	-0.001
1.000	1.00	1.000	0

Table 4.3. Typical effect of an offset of 0.147 V (0.015 ppm)

V_R	Meter Reading SO_2 (ppm)	Actual (ppm)	Error (ppm)
0.147	0.015	0.000	Not Applicable
0.206	0.020	0.013	+0.007
0.288	0.030	0.026	+0.004
0.346	0.040	0.037	+0.003
0.392	0.050	0.048	+0.002
0.533	0.100	0.100	0
0.673	0.200	0.199	+0.001
0.756	0.300	0.300	0
0.859	0.500	0.499	+0.001
0.928	0.700	0.701	-0.001
1.000	1.000	0.999	+0.001

4.7 SUMMARY OF FPD ANALYZER PARAMETERS WHICH MUST BE OPERATOR-CONTROLLED

Operator-controlled parameters relating to the operation of an ambient air SO_2 FPD analyzer are summarized in Table 4.4. The table lists the parameter, how the operator controls the parameter, how the operator may identify lack of control of the parameter, and how the operator may bring the parameter into control.

Table 4.4 FPD analyzer parameters which must be operator-controlled in order to obtain valid data

---

PARAMETER

Air sample flow rate, cc/minute

How Operator Controls Parameter

Needle Valve. (NOTE: Monitor Labs Model 8450 and Meloy Model 285 have a preset control which operator cannot adjust.)

How Operator May Identify Lack of Control

1. Test airflow to sample inlet with calibrated bubble flowmeter or calibrated mass flowmeter. After correction to 760 mm Hg, 25°C, compare to previous determination and/or manufacturer's setting.

2. Check the instrument's calibrated air rotameter and compare setting with that found at last calibration. (NOTE: Most air rotameters measure zero air from internal source and not the actual sample flow; therefore, use flowmeter check in addition to rotameter check.) After long periods of use, rotameters may exhibit "sag." The rotameter ball will move to a new location, but the same flow rate will continue. This is caused by a combination of electrostatic effects and scratching of the rotameter column by the rotameter float.

How Operator May Bring Parameter Into Control

1. Remove any obstructions to flow. (Dirty Teflon filter, dirty, kinked, or bent Teflon tubing, dirt-plugged orifice, defective Teflon solenoid valve, plugged or bent exhaust line, plugged dilution air inlet orifice and/or filter, Teflon tubing squeezed shut by compression fitting, etc.)

2. Eliminate any leaks in sample flow system. (Ill-fitting particulate filter, loose compression fitting, loose or poor connection of sampling line to sampling manifold, leaking solenoid valve, loose connection to sampling pump, etc.)

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

How Operator May Bring Parameter Into Control (continued)
3. Verify sample pump performance. (Sample pumps periodically need new diaphragms or valve assemblies. Dust particles can affect the flow and the flow will vary with length of pump operation.)
4. Check burner assembly components for water vapor condensation and corrosion. (Verify heater operation and clean or replace corroded components.)

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Hydrogen flow rate, cc/minute

How Operator Controls Parameter

Hydrogen pressure regulator and gauge. (Some older analyzers have a needle valve control or a pressure regulator with no gauge. These adjustments are in addition to the pressure regulator and gauge located at the hydrogen tank or generator.)

How Operator May Identify Lack of Control

1. Check the instrument's calibrated H_2 rotameter and compare setting with that found at last calibration, and/or with manufacturer's suggested setting. Be certain the rotameter is not "sticking."

2. Disconnect hydrogen feed at burner assembly, override the hydrogen shutoff control, and measure flow with bubble flowmeter or calibrated hydrogen mass flowmeter. (Caution! Hydrogen is a flammable gas; provide adequate ventilation.) Compare with previously determined H_2 flow rates.

How Operator May Bring Parameter Into Control

1. Check hydrogen source (cylinder or generator) for adequate pressure and pressure setting.

2. Be certain H_2 solenoid is not sticking shut.

3. Check for obstructions to flow (bent metal tubing). Check for leaks with leak detector solution.

4. Check burner assembly for corrosion.

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Interferences to SO_2 Detectability

1. Sulfur compounds other than SO_2
2. Carbon dioxide
3. Water condensation
4. Stainless steel or plastic tubing in sampling line
5. SO_2 removed in the presence of O_3 in heated H_2S silver scrubber

How Operator Controls Parameter

1. The positive interference of sulfur compounds other than SO_2 is eliminated by use of a scrubber which is available from the instrument manufacturer. Determine or estimate the average concentration of H_2S for the area in ppm. Use the manufacturer's ppm-hours rating of scrubber to compute expected lifetime for the area.

2. The negative interference of carbon dioxide is minimized by calibration with air containing ambient levels of CO_2. (Refer to discussion of clean air supplies for FPD calibration, Section 3.3.)

3. The negative effect of water condensation in manifold and sampling lines is minimized by proper temperature and humidity control of the room housing the analyzer.

4. Stainless steel, rubber, polyethylene, etc., tubing is never used as a sample line since SO_2 absorbs and reacts. Use only Teflon.

5. Keep H_2S scrubber temperature as low as possible to obtain optimum performance. Instruments equipped with unheated scrubbers show less interference.

How Operator May Identify Lack of Control

1. Challenge the scrubber with a low level of H_2S and check for analyzer response. If response occurs, scrubber is not effective.

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

How Operator May Identify Lack of Control (continued)

2. Perform independent calibration check (make no adjustments) of analyzer with calibration system known to have ≅350 ppm CO_2 present. Compare calibration curves and see if the analyzer's response has diminished. (Refer to Section 3.0, Effects of CO_2.)

3. SO_2 concentration at time of pre-calibration check is lower than expected. Visible moisture present in sample line or station manifold.

4. Inspect analyzer and sampling lines for proper material (Teflon).

5. Challenge analyzer with SO_2, then with SO_2 plus O_3.

How Operator May Bring Parameter Into Control

1. Replace or clean the scrubber according to manufacturer's instructions.

2. Perform calibration with ambient level of CO_2 present in the calibration gas. (See Section 5.0 for a procedure for determination of ambient levels of CO_2.)

3. Maintain high enough room temperature such that H_2O condensation does not occur.

4. Replace steel or plastic tubing with Teflon tubing.

5. Use unheated H_2S scrubber. Check temperature control of heated scrubber.

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Temperatures

1. Shelter temperature

2. Temperature of analyzer components (photomultiplier tube housing, burner block, and exhaust assembly, H_2S scrubber)

How Operator Controls Parameter

1. Adjust heating/air conditioning controls or shelter.

2. Operator cannot control temperatures of analyzer components.

How Operator May Identify Lack of Control

1. Shelter temperature is outside the limits of 20-30°C (68-86°F).

2. The following may indicate lack of instrument temperature control.

   a. Zero or span signal is unsteady. Photomultiplier tube housing temperature may be varying. This affects the PMT output and H_2 flow controlling capillaries or other pneumatic impedance elements. Check for proper temperature by use of built-in thermocouple or status light of analyzer.

   b. Flame will not light, or moisture droplets appear in exhaust line. This may indicate that the burner block and exhaust manifold have lost heat and allowed condensation to occur. Check thermocouple or status light. Touch burner block and exhaust lines cautiously. They should be very hot.

   c. H_2S scrubber fails to scrub H_2S. This could indicate failure of heater element in scrubber.

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued

How Operator May Bring Parameter Into Control
1. Adjust shelter temperature.
2. Replace defective heaters.

Table 4.4. FPD analyzer parameters which must be operator-controlled in order to obtain valid data (continued)

PARAMETER

Linearity of signal output

How Operator Controls Parameter

Adjustments of Linearization Electronic Circuitry. CAUTION! Do not adjust without first determining this is truly the problem. (NOTE: the linearization circuitry is factory-set for the Monitor Labs Model 8450 and cannot be operator-adjusted.)

How Operator May Identify Lack of Control

Operator performs multipoint calibration and examines graphical plot of analyzer response for departures from linearity. (Refer to Calibration Section 4.0 and Linearization Procedures, in the manufacturer's instruction manual.)

How Operator May Bring Parameter Into Control

Operator generates SO_2 calibration gases (zero, span, and intermediate points) and adjusts linearization circuitry until linearity is achieved. (See Linearization Procedures in the manufacturer's instruction manual.) The use of a picoamp source to generate amperage signals equal to those expected from SO_2 is another approach to establishing linearity (consult manufacturer).

Concluded

SECTION 5.0
PROCEDURAL AIDS

5.1 INTRODUCTION

Establishing and maintaining sample and calibration gas flow rates is essential to obtaining quality data from any ambient air analyzer. Procedures, explanations, and precautions for determining and correcting airflows are given in this section.

A common piece of equipment for determining the volumetric flow of a gas is the soap film flowmeter or bubble flowmeter (Section 5.2). Such flowmeters can be bought commercially or built in glassblowing shops. All soap film flowmeters should be calibrated by water displacement or by comparison to a certified soap film whose volume is traceable to NBS standards of volume. An example of a certified soap film flowmeter is the Hastings Model HBM-1 which is available from the Hastings Raydist Company, Hampton, Virginia.

Section 5.3 discusses the use and care of the mercury barometer which is used to determine atmospheric pressure. Section 5.4 discusses the use of a water manometer which is used to determine very slight variations in pressure. Section 5.5 discusses an equation to correct volumetric flow rates to the normal conditions of 25° C and 760 mm Hg.

Section 5.6 outlines a quantitative method for determining the CO_2 content of ambient air or air from clean air supplies.

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5.2 SOAP FILM FLOWMETER, SFFM, OR BUBBLE FLOWMETER

	PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
1.	Choose the size SFFM needed for the job. Be certain it is calibrated or certified.[19] See Figure 5.1	If flowmeter volume is too small, one cannot accurately time the soap film movement. About 30-60 seconds time for measurements is desirable.	If gas flow rate is less that 2 cc/minute, gas diffusion through soap film is appreciable. Do not use SFFM for very low flow measurements.
2.	Place SFFM on level spot and secure it to prevent tipping.	Inaccurate readings may be obtained if SFFM is not level. A ringstand with soft clamps is a convenient holder.	Do not over-tighten clamps.
3.	Fill reservoir with soap solution.	A liquid leak detector, such as "SNOOP®" is suggested.	Fill reservoir and lines to a point just below lower air inlet to SFFM.
4.	Connect SFFM to gas tubing of flowing system. a. If source pushes gas out, connect to lower port of SFFM (upper port open). b. If source pull gas in, connect to upper port of SFFM (lower port open). c. If measuring an inline flow, break into system and connect both ports, making closed loop.	Leak-free connection is essential. Use one of the following: a. Ground glass ball/socket fittings and clamp. b. Compression fittings with soft rubber or Teflon gaskets. c. Smaller tubing forced tightly into or over larger tubing.	Double check the direction of air flow. If soap solution is pulled into an instrument it may be ruined. Use of an inline liquid trap is suggested. Be cautious when measuring toxic or flammable gases. Provide ventilation to the outside via 6.3 mm (1/4 in.) tubing. Work in a fume hood.

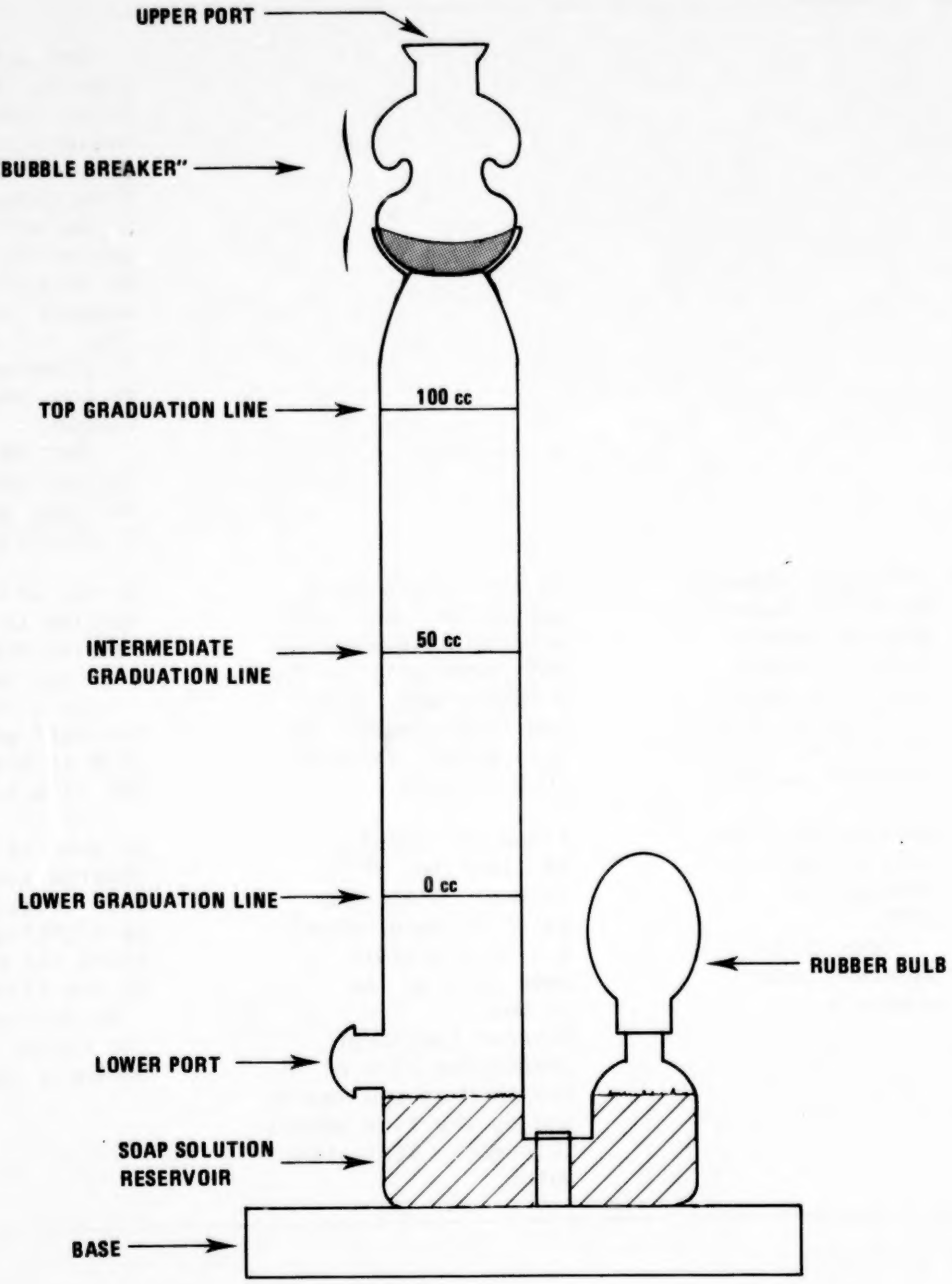
UPPER PORT
"BUBBLE BREAKER"
TOP GRADUATION LINE
100 cc
INTERMEDIATE GRADUATION LINE
50 cc
LOWER GRADUATION LINE
0 cc
RUBBER BULB
LOWER PORT
SOAP SOLUTION RESERVOIR
BASE

Figure 5.1. Soap film flowmeter.

PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
		Use sufficiently large inlet lines to avoid backpressure and flow change. Do not pressurize the SFFM by attaching an exhaust line that is too small in diameter and/or too long in length. When measuring inline, keep connections as short as possible.
5. Lift soap solution reservoir tube or depress rubber bulb to create soap film bubble. Release 10 to 20 bubbles to wet interior surface.	As the liquid rises above the lower port of SFFM, air entering this port will create a bubble and carry the film upward. At this point, release tube or bulb.	Do not allow the bubbles to be carried into the instrument. Use a "bubble breaker" atop the SFFM to break the film surface.
6. Measure the flow rate of gas through the SFFM. Take three separate measurements.	Allow all bubbles to clear the SFFM column. With stopwatch in hand, start a single uniform soap film up the column. Observe the lower graduation line of the SFFM at eye level and as the film passes this mark, start the watch.	Be sure to observe soap film travel by sighting along the plane of the film. Do not touch the rubber bulb during a reading.

5.2 SOAP FILM FLOWMETER, SFFM, OR BUBBLE FLOWMETER (con.)

PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
	Stop the watch when the soap film crosses the top graduation or some known intermediate graduation.	
7. Compute the volumetric flow rate. Average the three values to obtain final value. Record all data calculations in notebook.	Divide the volume of the flowmeter (or the volume traversed), cc, by the time required, minutes. Example calculation: Soap film traverses 100 cc in 39 seconds. $\frac{39 \text{ sec}}{60 \text{ sec/min}} = 0.65 \text{ min}$ $\frac{100 \text{ cc}}{0.65 \text{ min}} = 153.8 \text{ cc/min}$ is the uncorrected volume flow rate.	If necessary for comparison, this volumetric flow rate should be corrected to standard temperature (25° C) and pressure (760 mm Hg). Also correct for water vapor pressure. See Section 5.5.
8. Disconnect SFFM from and gas source.		Be certain that all disconnected fittings, etc. are retightened and leak-tested.

5.3 MERCURY COLUMN BAROMETER, FORTIN TYPE

	PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
1.	Assure that the barometer is mounted properly, and that the mercury is clean.	Barometer should be wall-mounted vertically and be perpendicular to a level floor. Dirty mercury is dull, tarnished.	If barometer is not level or mercury is dirty, erroneous readings are obtained. Return to factory if mercury column contains dirty mercury.
2.	Adjust mercury reservoir leveling screw so liquid mercury just touches sharp point of ivory zero point.	This adjusts the level of mercury in the cistern to the same point for each reading. A flashlight provides helpful illumination. Adjust until the zero pointer makes a slight "dimple" in the mercury pool, then "back-off" slightly.	Do not force or strain the adjusting screw.
3.	Locate the top of the mercury column, then tap the barometer case lightly with fingers.	The height of the mercury meniscus (the curvature of the mercury surface inside a glass tube) is greater on a rising barometer than a falling one. Tapping brings the meniscus to an average height.	
4.	Adjust vernier plate with notched wheel until lower edge of vernier is in same plane as top of mercury meniscus.	This process locates the top of the mercury column.	When reading barometer, the reader's eye should be in the same horizontal plane as the top of the meniscus and the lower edge of the

PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
		vernier plate. Line your sight on the bottom of vernier and the metal vernier guide located behind the mercury column.
5. Determine reading in English or metric units. a. Read column height. b. Read fractional value from venier scale.	To read column height, determine scale value that lower line of venier intercepts or is just above. Read venier by determining which one of the 9 division marks (1 to 9) intersects most closely with scale value lines. Example: Lower line of vernier "crosses" between 755 and 756 mm Hg. This says the reading is between 755 and 756 mm Hg. The vernier line marked "8" matches exactly with the 771 mm line of the scale. Thus, the uncorrected barometric pressure is 755.8 mm Hg.	
6. Apply corrections for the temperature of the barometer, and if desired, gravity.	Temperature affects the expansion of mercury and the scale metal.	If it is desired convert an English reading to a metric reading or vice

PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
Use the corrected pressure reading to calculate gas volumes at standard temperatures and pressure.	Temperature correction tables and ininstructions for their use for English and metric scales accompany the barometer or may be found in such publications as the *Handbook of Chemistry and Physics*. Take the temperature reading from the thermometer attached to the barometer or from a therometer in the same area.	versa, always apply the temperature and gravity corrections *before* making the conversion.

5.4 WATER MANOMETER, U-TUBE

PROCEDURE	RESULTS, EXPLANATION	PRECAUTION
1. Choose a U-Tube water or oil manometer. See Figure 5.2		Manometers using liquids other than water (such as red oil) will have graduations different from H_2O manometers. Be sure to use the correct fluid.
2. Level the manometer so liquid levels in both sides of the "U" are the same.		
3. Attach, by use of rubber tubing, one side of the "U" to the manifold or other item for which the pressure differential is desired.	As the moving gas stream sweeps by, a slight vacuum may be created. If the manifold is pressurized, a positive pressure will be shown.	Leave the other side of the "U" open to the atmosphere.
4. Read the manometer establish ΔP, inches of H_2O or cm of H_2O.	Read the difference in heights of the water level in the two sides of the "U". See Figure 5.2	If greater than 1 to 2 inches H_2O pressure is noted, the FPD zero stability may be affected. Rework any calibration manifolds which display such characteristics.

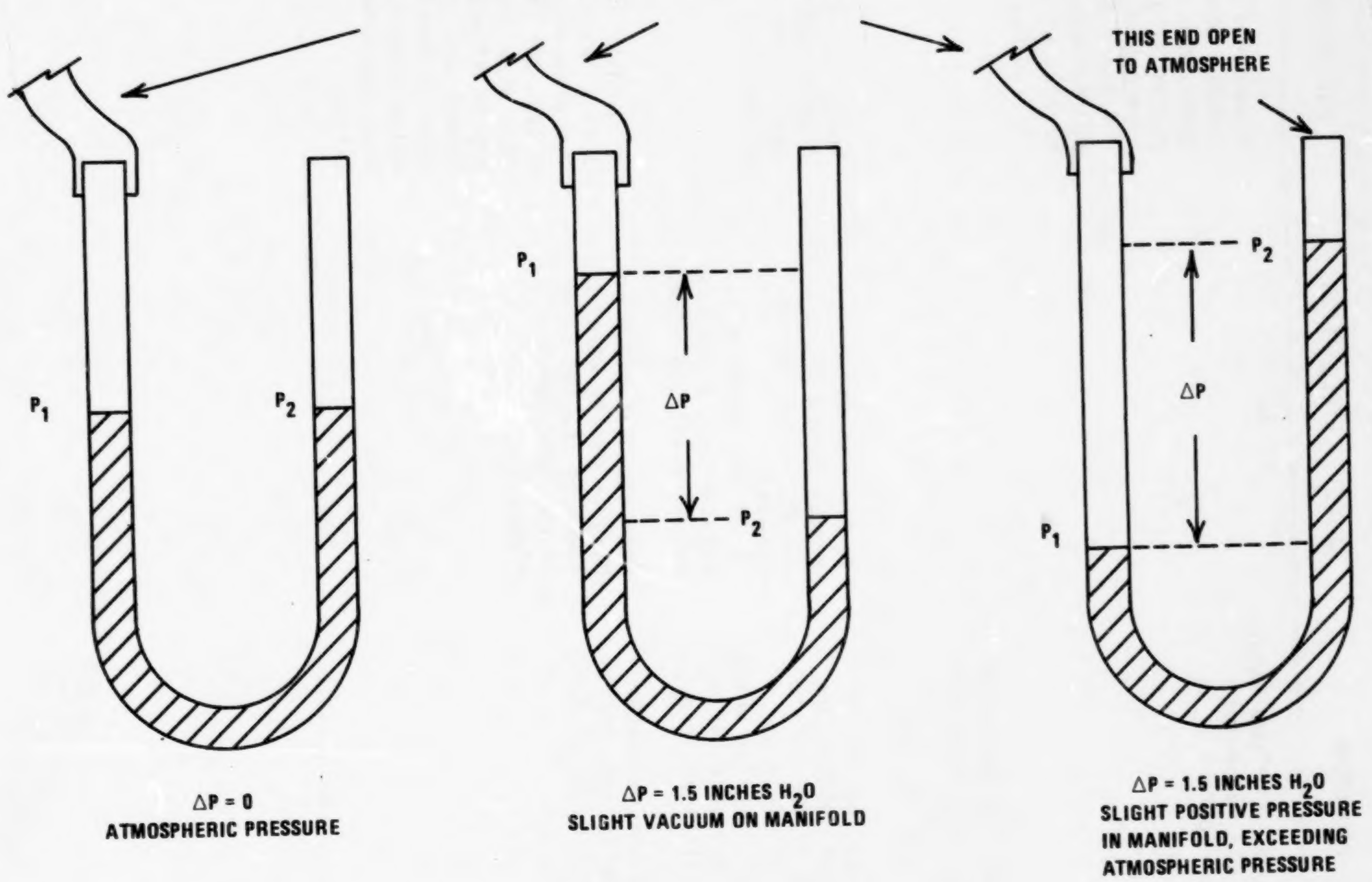
TUBE CONNECTED TO PORT OF MANIFOLD, ETC.
THIS END OPEN TO ATMOSPHERE
P_1
P_2
$\Delta P = 0$
ATMOSPHERIC PRESSURE
P_1
ΔP
P_2
ΔP = 1.5 INCHES H_2O
SLIGHT VACUUM ON MANIFOLD
P_2
ΔP
P_1
ΔP = 1.5 INCHES H_2O
SLIGHT POSITIVE PRESSURE IN MANIFOLD, EXCEEDING ATMOSPHERIC PRESSURE

Figure 5.2. Water manometer, "U" tube.

5.5 STEPS FOR CORRECTING AIRFLOW TO STANDARD TEMPERATURE AND PRESSURE

In air pollution work, the standard temperature is 25° C; the standard pressure is 1 atmosphere or 760 mm Hg (29.92 inches Hg). Almost all flow measurements taken by volumetric displacement methods must be corrected to standard temperature and pressure for comparisons to other work. Soap film flowmeter and wet test meter measurements must also be corrected for the effect of water vapor. Table 5.1 lists the vapor pressure of water (mm Hg) at various temperatures.

Apply this equation to correct flows:

$$F_s = F \times \frac{P - P'}{760} \times \frac{298.15}{t + 273.15}$$

where:

F_s = flow rate at standard conditions in liters/minute

F = measured flow rate in liters/minute by displacement

P = barometric pressure in mm Hg

P' = vapor pressure of water, mm Hg, at temperature t.

t = air temperature, degrees C

For an example calculation using this equation, refer to Section 3.4.4.

5.6 ASCARITE® METHOD FOR CO_2 DETERMINATION

Average levels of CO_2 in ambient air or in air from clean air sources can be determined gravimetrically by adsorption and reaction of CO_2 on Ascarite. The increase in the weight of the tube containing the Ascarite can be related to the CO_2 concentration.

This method is based on the instructions given in the APHA manual, Methods of Air Sampling and Analysis, "Tentative Method for Preparation of Carbon Monoxide Standard Mixtures," p. 224, 1972.

Ascarite is available from most laboratory supply houses. A mesh of 8-20 is specified for this procedure. As Ascarite collects CO_2, its color changes from brown to white due to sodium carbonate formation.

Table 5.1. Vapor pressure of water at various temperatures, mm Hg

Temp. °C	0.0	0.2	0.4	0.6	0.8
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737
40	55.324	55.91	56.51	57.11	57.72
41	58.34	58.96	59.58	60.22	60.86
42	61.50	62.14	62.80	63.46	64.12
43	64.80	65.48	66.16	66.86	67.56
44	68.26	68.97	69.69	70.41	71.14
45	71.88	72.62	73.36	74.12	74.88
46	75.65	76.43	77.21	78.00	78.80
47	79.60	80.41	81.23	82.05	82.87
48	83.71	84.56	85.42	86.28	87.14
49	88.02	88.90	89.79	90.69	91.59
50	92.51	93.5	94.4	95.3	96.3
51	97.20	98.2	99.1	100.1	101.1
52	102.09	103.1	104.1	105.1	106.2
53	107.20	108.2	109.3	110.4	111.4
54	112.51	113.6	114.7	115.8	116.9
55	118.04	119.1	120.3	121.5	122.6
56	123.80	125.0	126.2	127.4	128.6
57	129.82	131.0	132.3	133.5	134.7
58	136.08	137.3	138.5	139.9	141.2
59	142.60	143.9	145.2	146.6	148.0

Source: *Handbook of Chemistry and Physics,* 50th Ed. The Chemical Rubber Co., Cleveland, Ohio.

5.6.1 Procedure

Loosely pack the Ascarite into 15 to 20 cm length (6 to 8 in.) glass or plastic tubes having a 1.27 cm (0.5 in) inside diameter. Plug the ends with glass wool and cap to protect from moisture. Carefully weigh the tube on an analytical balance to the nearest milligram. Do the same with a tube containing Drierite.

Set up a sampling train similar to the one shown in Figure 5.3.

Determine the flow rate into the Ascarite cartridge. 500-1000 cc/min is a reasonable flow.

Collect air for a sufficient length of time to obtain an accurate weight difference; about 30-60 minutes. Express the total flow volume in cubic meters at STP; express the weight gain in micrograms. Compute the ppm value of CO_2.

Example calculation:

Air flow rate = 500 cc/min at STP (25° C, 760 mm Hg)

Time = 30 minutes

Total weight gain = 0.0094 grams (9400 μg)

(total weight gain = Ascarite tube gain + Drierite tube gain)

Thus:

$$0.5 \text{ liters/min} \times 30 \text{ min} = 15 \text{ liters} = 0.015 \text{ m}^3$$

$$\frac{9400 \ \mu g}{0.015 \ m^3} = \frac{X \ \mu g}{1 \ m^3}$$

$$X = 626667 \ \mu g$$

Therefore, since 1798 μg/m^3 CO_2 = 1 ppm CO_2 at STP

$$CO_2, \text{ ppm} = \frac{626667}{1798} = 348 \text{ ppm}$$

In field use, this Ascarite CO_2 collection system has been shown to have an accuracy of 5 percent or better and a precision of ±12 ppm for co-located sampling systems.[22]

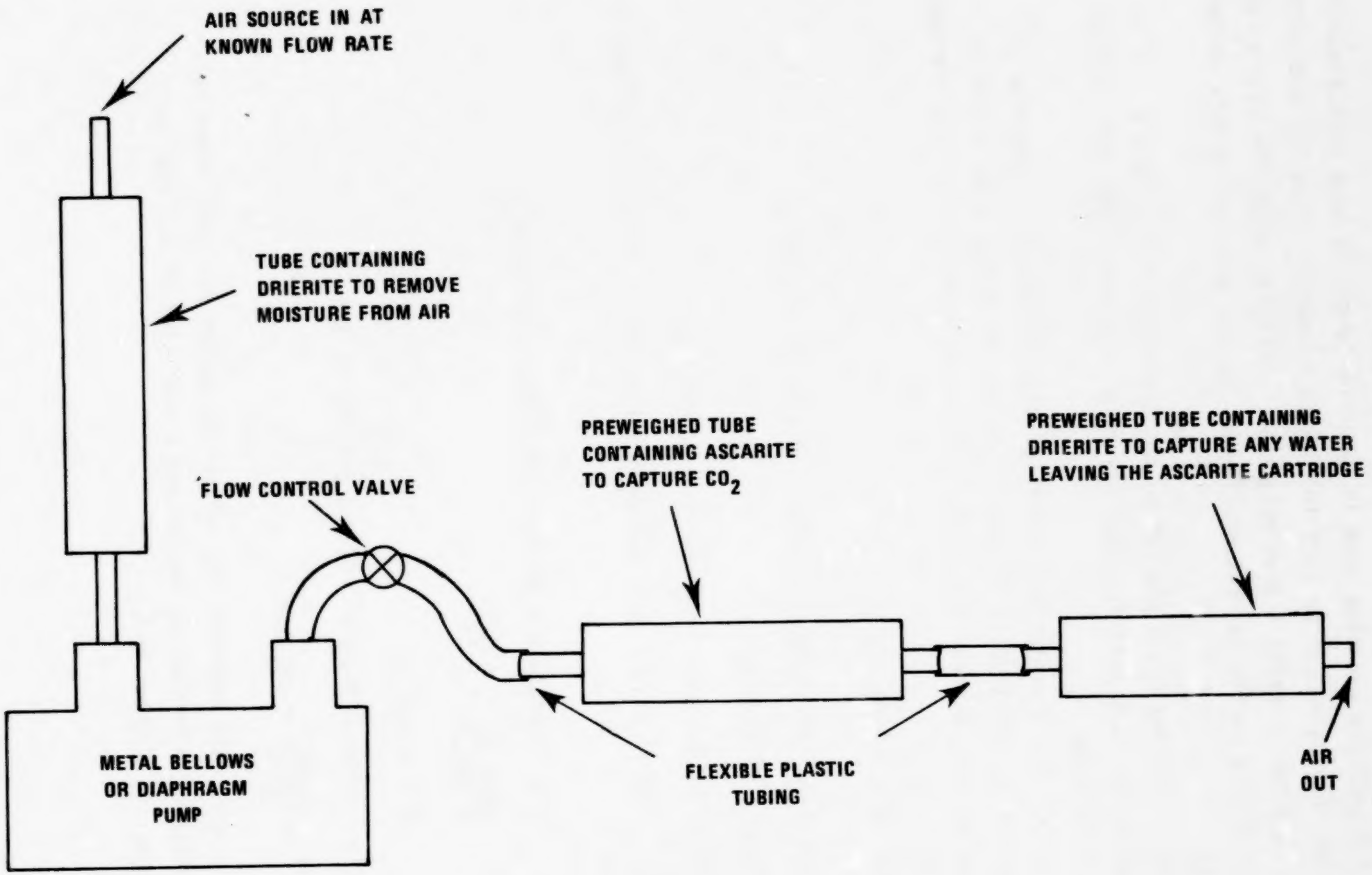
AIR SOURCE IN AT
KNOWN FLOW RATE
TUBE CONTAINING
DRIERITE TO REMOVE
MOISTURE FROM AIR
FLOW CONTROL VALVE
PREWEIGHED TUBE
CONTAINING ASCARITE
TO CAPTURE CO2
PREWEIGHED TUBE CONTAINING
DRIERITE TO CAPTURE ANY WATER
LEAVING THE ASCARITE CARTRIDGE
METAL BELLOWS
OR DIAPHRAGM
PUMP
FLEXIBLE PLASTIC
TUBING
AIR
OUT

Figure 5.3. Ascarite sampling train for CO_2 determination.

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